Supporting Information for

Single-atomic-site cobalt stabilized on nitrogen and phosphorus co-doped carbon for selective oxidation of primary alcohols

Shufang Ji,[a] Yuanjun Chen,[a] Zedong Zhang,[a] Weng-Chon Cheong,[a] Zirui Liu,[a] Dingsheng Wang,[a] and Yadong Li[a]*

[a]Department of Chemistry, Tsinghua University, Beijing 100084, China.

EXPERMENTIAL DETAILS

Chemicals: Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, analytical grade, 98%, Alfa Aesar), Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, analytical grade, 98%, Sinopharm Chemical), 2-methylimidazole (analytical grade, 98%, Alfa Aesar), phosphonitrilic chloride trimer (analytical grade, 98%, Alfa Aesar), bis(4-aminophenyl) ether (analytical grade, 98%, Alfa Aesar), methanol (analytical grade, Sinopharm Chemical), and triethylamine (analytical grade, Sinopharm Chemical) were used without any further purification.

Synthesis of ZnCo-ZIF-68, ZIF-8 and ZIF-67: In a typical synthesis of ZnCo-ZIF-68, $Zn(NO_3)_2 \cdot 6H_2O$ (5.67 g) and $Co(NO_3)_2 \cdot 6H_2O$ (50 mg) were dissolved in 150 mL methanol. 2-methylimidazole (6.58 g) was also dissolved in 150 mL methanol. Subsequently, two solutions were mixted with vigorous stirring for 3 min at room temperature. Then the as-obtained mixed solution was transfer to the sealed container, and placed it into the constant temperature oven at 60 °C for 6 h. The as-prepared precipitates were centrifuged, washed and dried at 80 °C. ZIF-8 was prepared with the same synthesis procedure of ZnCo-ZIF-68 except that $Co(NO_3)_2 \cdot 6H_2O$ was not added. ZIF-67 was prepared with the same synthesis procedure of ZnCo-ZIF-68 except that $Zn(NO_3)_2 \cdot 6H_2O$ (5.67 g) was substituted by $Co(NO_3)_2 \cdot 6H_2O$ (5.55 g).

Synthesis of ZnCo-ZIF-68@PZM and ZIF-8@PZM: In a typical synthesis of ZnCo-ZIF-68@PZM, bis(4-aminophenyl) ether (640 mg) and triethylamine (16.8 mL) was dissolved in 200 mL of methanol. And the as-obtained powder of ZnCo-ZIF-68 (800 mg) was dissolved in 40 mL of methanol. Subsequently, the above two solutions were mixted to from a homogeneous solution for 10min. Then, phosphonitrilic chloride trimer (320 mg) was dissolved in 100 mL of methanol and was added to the above homogeneous solution. After finishing, the homogeneous dispersion was maintained at 40°C for 6 h. The as-prepared precipitates were centrifuged, washed and dried at 80 °C. ZIF-8@PZM was prepared with the same synthesis procedure of ZnCo-ZIF-68@PZM except that ZnCo-ZIF-68 (800 mg) was substituted by ZIF-68 (800 mg).

Synthesis of Co_1/P-NC, Co_1/ NC, P-NC and Co NPs/NC: The obtained powers of ZnCo-ZIF-68@PZM, ZnCo-ZIF-68, ZIF-8@PZM and ZIF-67 were placed in quartz boats, respectively, and then maintained 950 °C for 3 h in a tube furnace with a heating rate of 5 °C min^{-1} under flowing nitrogen atmosphere. When these samples cooled to room temperature, the as-prepared samples, Co_1/P-NC, Co_1/NC, P-NC and Co NPs/NC were respectively collected and without any treatment for further use.

Synthesis of M_1/P-NC: $Zn(NO_3)_2 \cdot 6H_2O$ (5.67 g) and metal nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, 69.4 mg; $Cu(NO_3)_2 \cdot 9H_2O$, 32.2 mg, respectively) were dissolved in 150 mL methanol. 2-methylimidazole (6.58 g) was also dissolved in 150 mL methanol. Subsequently, two solutions were mixted with vigorous stirring for 3 min at room temperature. Then the as-obtained mixed solution was transfer to the sealed container, and placed it into the constant temperature oven at 60 °C for 6 h. The as-prepared precipitates (marked as ZnFe-ZIF and ZnCu-ZIF, respectively) were centrifuged, washed and dried at 80 °C. The synthesis of ZnFe-ZIF@PZM or ZnCu-ZIF@PZM was prepared with the same synthesis procedure of ZnCo-ZIF-68@PZM except that ZnCo-ZIF-68 (800 mg) was substituted by ZnFe-ZIF@PZM or ZnCu-ZIF@PZM (800 mg), respectively. For the synthesis of

M_1/P-NC catalysts (M=Fe, Cu), the obtained powers of ZnFe-ZIF@PZM or ZnCu-ZIF@PZM composites were placed in quartz boats, respectively, and then maintained 950 °C for 3 h under flowing nitrogen atmosphere. When these samples cooled to room temperature, the as-prepared Fe_1/P-NC and Cu_1/NC catalysts were obtained.

Characterizations: X-ray powder diffractometer (XRD) (Rigaku RU-200b with Cu Kα radiation (λ = 1.5406 Å)) was performed to confirm the crystalline structure and phase purity. The X-ray photoelectron spectroscopy (XPS) data were recorded using a ULVAC PHI Quantera microscope. TEM images of samples were obtained to characterize the sizes and morphologies of on a Hitachi H-800 TEM. The high-resolution TEM and elemental mappings were collected on a JEOL JEM-2100F with electron acceleration energy of 200 kV. HAADF-STEM images were measured by using a JEOL 200F transmission electron microscope operated at 200 keV, equipped with a probe spherical aberration corrector. The Co concentrations of the samples were measured by ICP-OES (Optima 7300 DV). The X-ray absorption find structure (XAFS) spectra data were collected at 1W1B station in Beijing Synchrotron Radiation Facility (BSRF, operated at 2.5 GeV with a maximum current of 250 mA, Co K-edge) The XAFS data of Co_1/P-NC sample were collected at room temperature in fluorescence excitation mode using a Lytle detector. Co foil and Co_3O_4 were used as references and measured in a transmission mode using ionization chamber.

Measurements of catalytic performance: All reactions were performed in the 10 mL standard Schlenk tube. Benzyl alcohol or substituted benzyl alcohol (0.2 mmol, 1.0 equiv.), Co species catalysts (Co 0.01 equiv.; Co_1/P-NC, 26 mg; P-NC, 26 mg; Co NPs/NC, 2 mg; $Co(NO_3)_2\cdot 6H_2O$, 0.6 mg; respectively), H_2O_2 (125 μL, 2.0 equiv.) and toluene (2 mL) was heated at 110 ^{o}C and vigorously stirred (800 rpm) for 16 hours. After completion of reaction, reaction mixture was extracted with ethyl acetate (3×5ml). The yield was determined by GC using tridecane as an internal standard. The Co species sites of the catalysts were measured by ICP-AES experiments.

SUPPLEMENTARY FIGURES

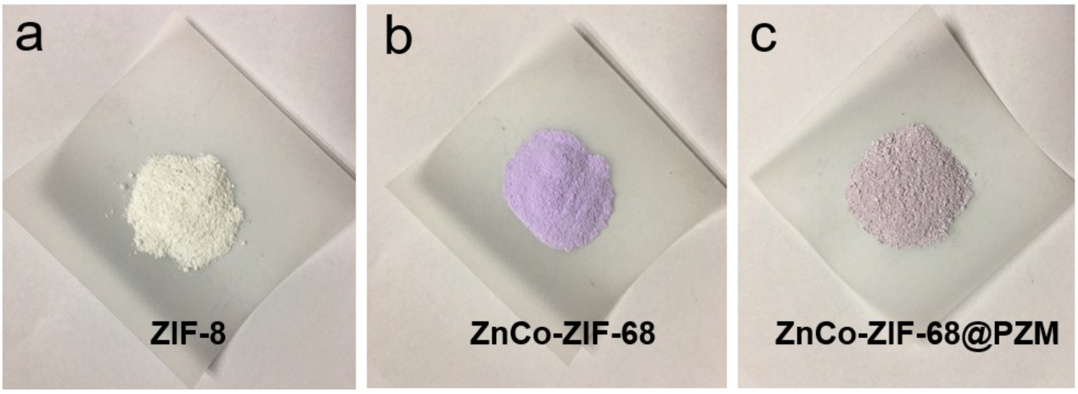


Figure S1. (a-c) The color of the samples obtained from ZIF-8, ZnCo-ZIF-68 and ZnCo-ZIF-68@PZM.

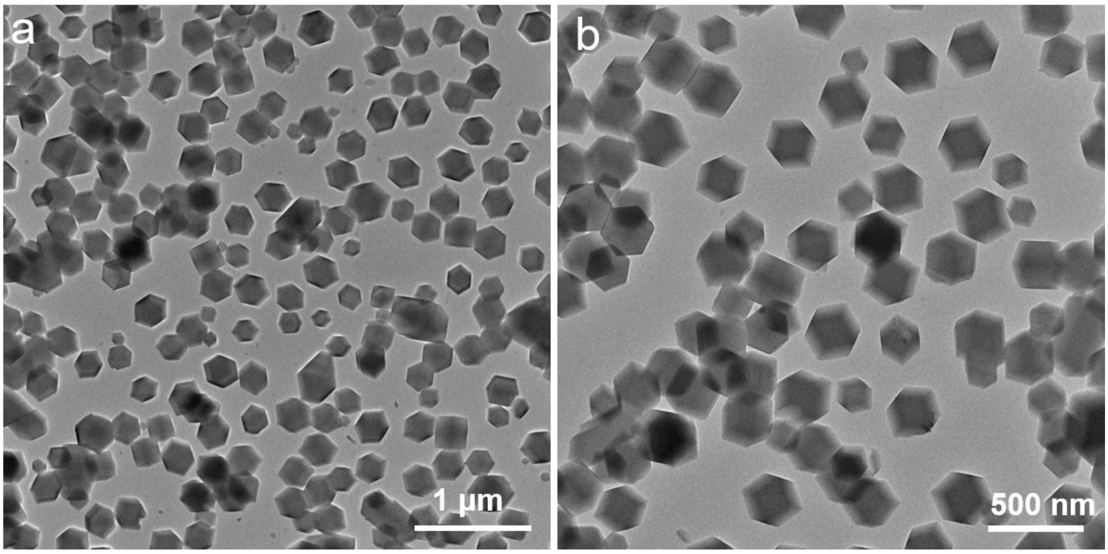


Figure S2. (a,b) TEM images of ZnCo-ZIF-68 (a) and ZIF-8 (b).

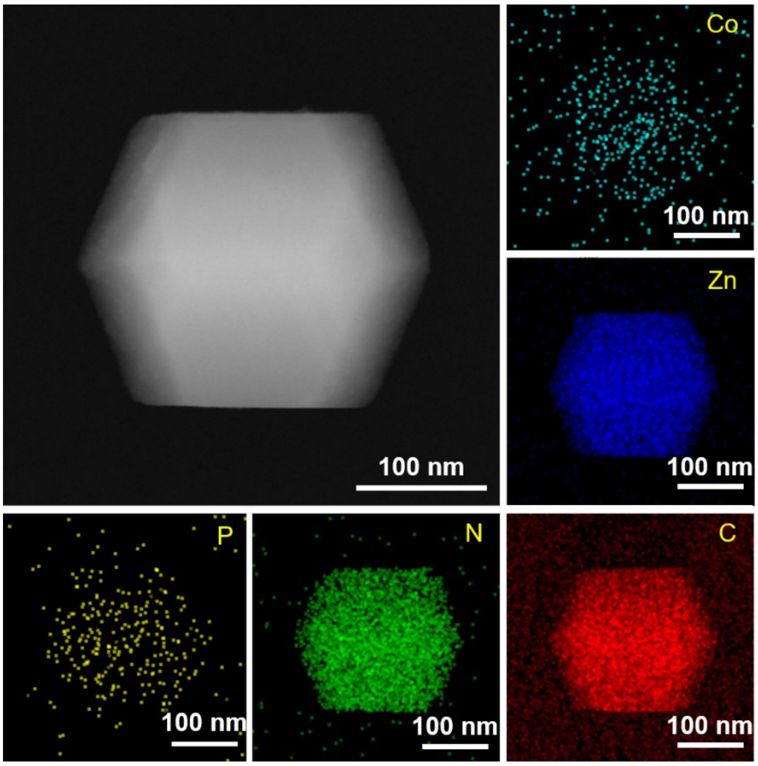


Figure S3. HADDF-STEM and the corresponding EDS mappings of the ZnCo-ZIF-68@PZM.

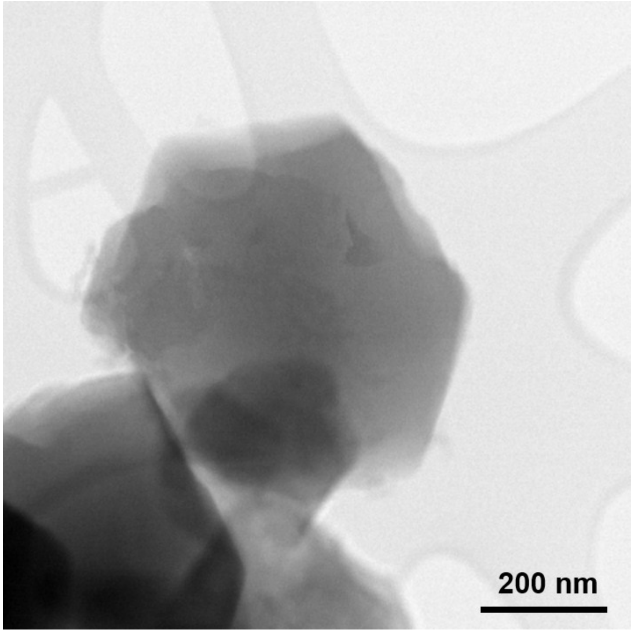


Figure S4. HRTEM image of the Co_1/P-NC catalyst.

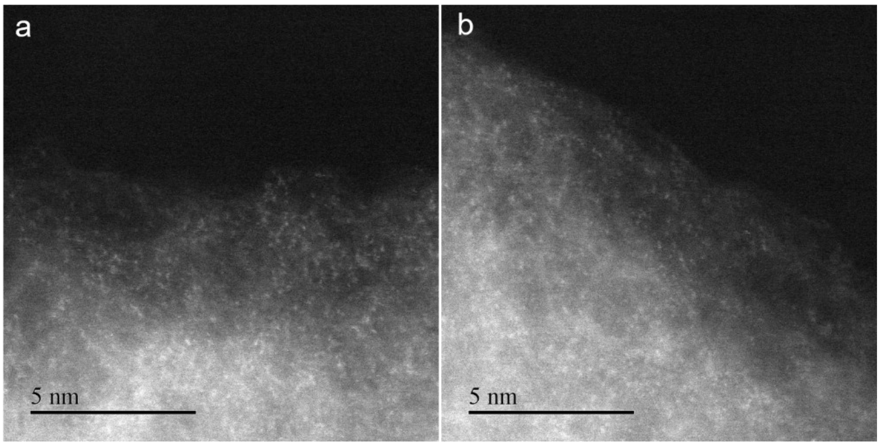


Figure S5. (a, b) AC HAADF-STEM images of the Co_1/P-NC catalyst in other different regions.

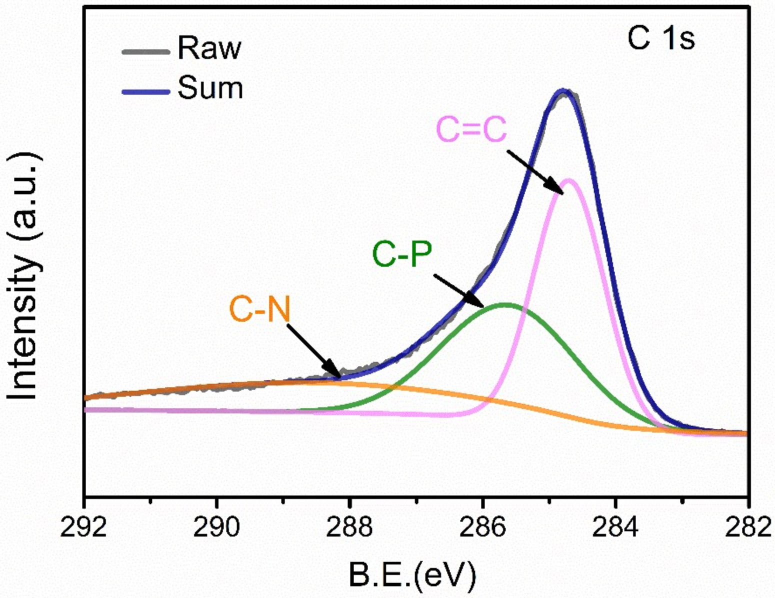


Figure S6. The C 1s spectrum of the Co_1/P-NC catalyst.

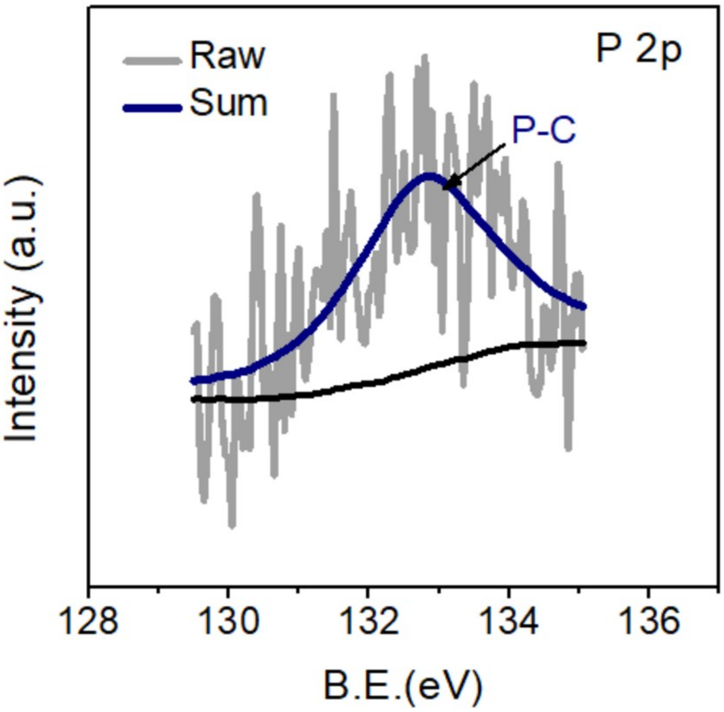


Figure S7. The P 2p spectrum of the Co_1/P-NC catalyst.

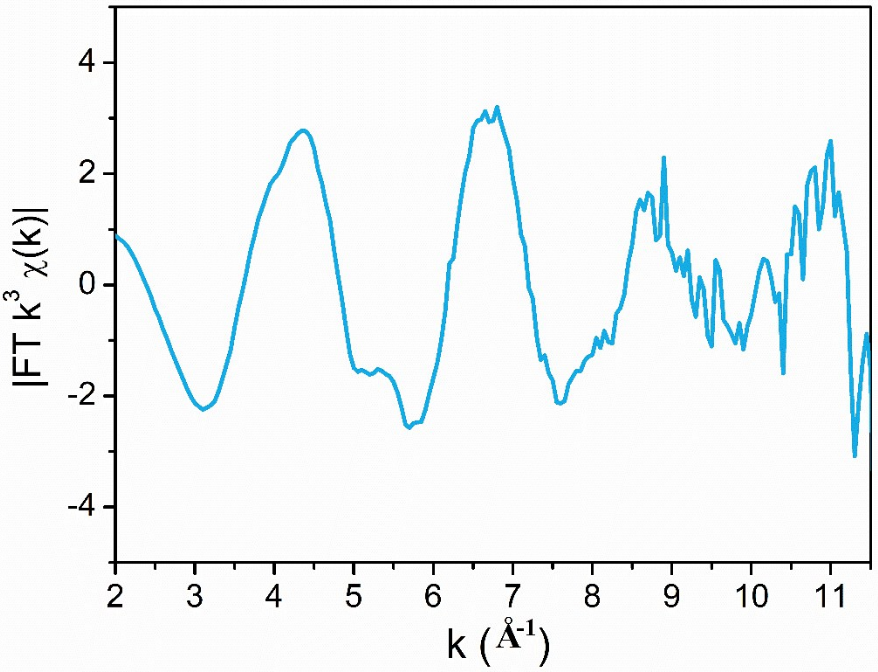


Figure S8. EXAFS k space of the Co_1/P-NC catalyst.

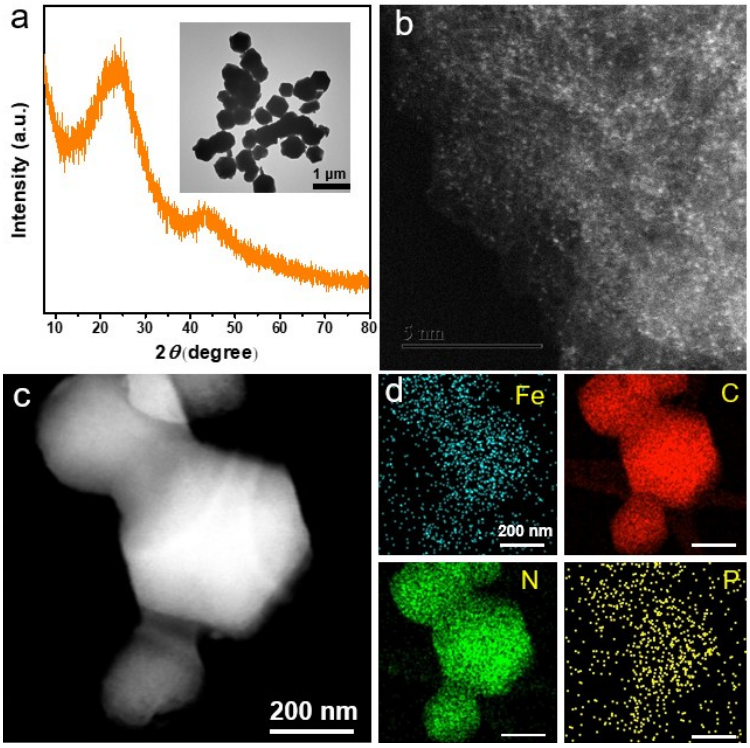


Figure S9. (a) XRD pattern and TEM image (inset) of the Fe_1/P-NC catalyst. (b) AC HAADF-STEM image, (c) HAADF-STEM image and (d) corresponding EDS element maps (Fe: cyan, C: red, N: green, P: yellow) of the Fe_1/P-NC catalyst.

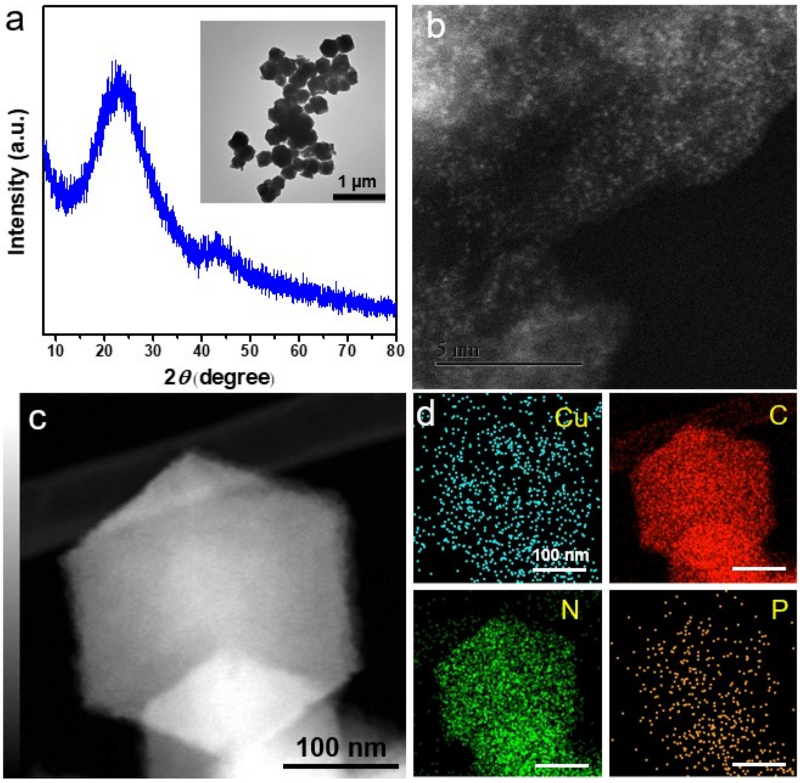


Figure S10. (a) XRD pattern and TEM image (inset) of the Cu_1/P-NC catalyst. (b) AC HAADF-STEM image, (c) HAADF-STEM image and (d) corresponding EDS element maps (Cu: cyan, C: red, N: green, P: orange) of the Cu_1/P-NC catalyst.

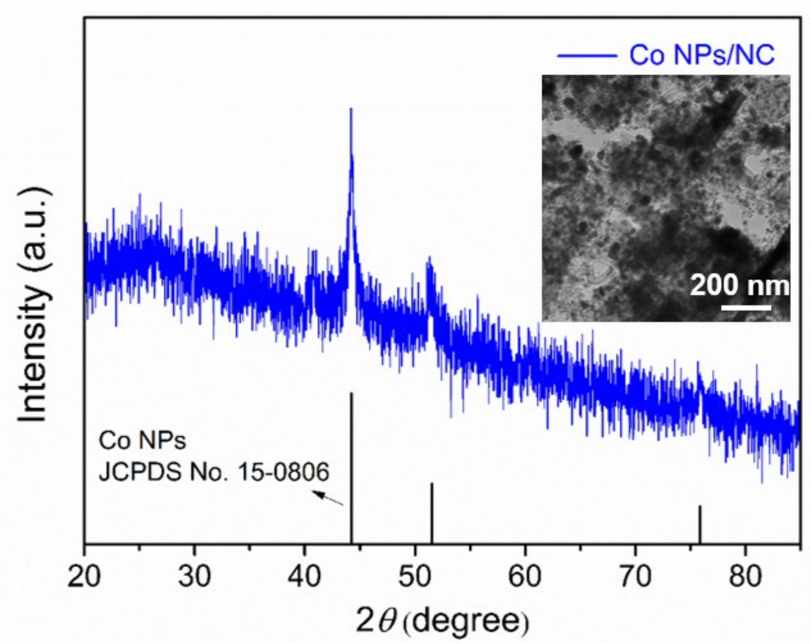


Figure S11. XRD pattern of Co NPs/NC (Inset: TEM image).

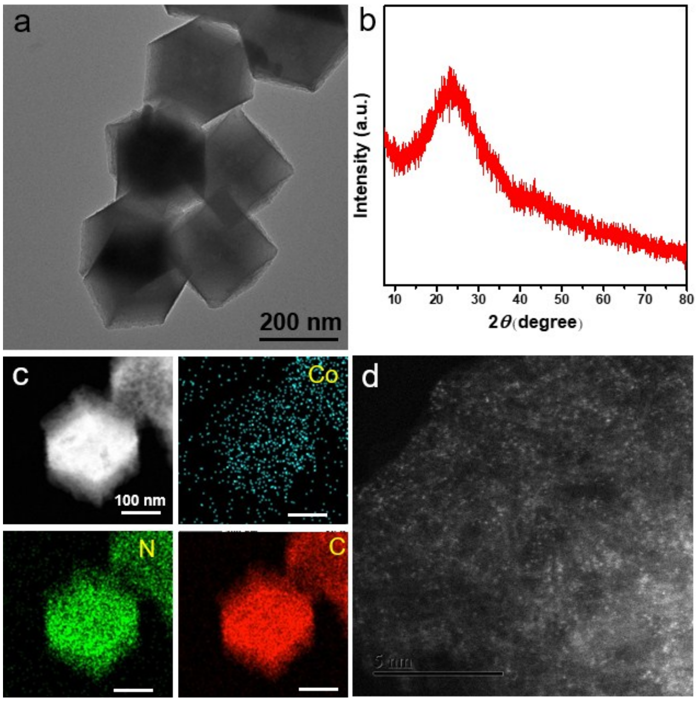


Figure S12. (a) TEM and (b) XRD pattern of the Co_1/ NC catalyst. (c) HAADF-STEM and corresponding EDS images of the Co_1/ NC catalyst. Co (cyan), C (red) and N (green). (d) AC HAADF-STEM image of the Co_1/ NC catalyst. The scale bar is 5 nm.

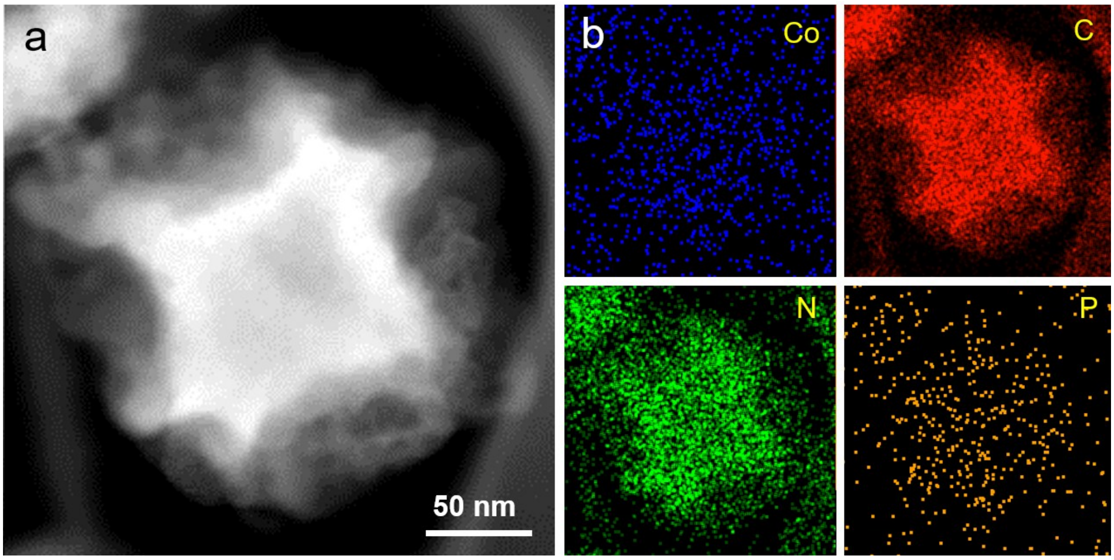


Figure S13. (a) The HAADF-STEM and (b) corresponding EDS mappings of the used Co_1/P-NC catalyst.

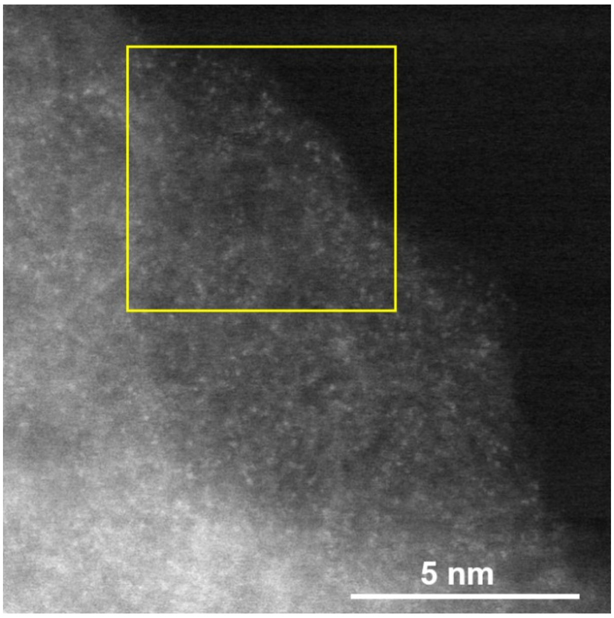


Figure S14. The aberration-corrected HAADF-STEM image of the used Co_1/P-NC catalyst. The enlarged aberration-corrected HAADF-STEM image in the yellow square box was shown in the inset of Figure 4b.

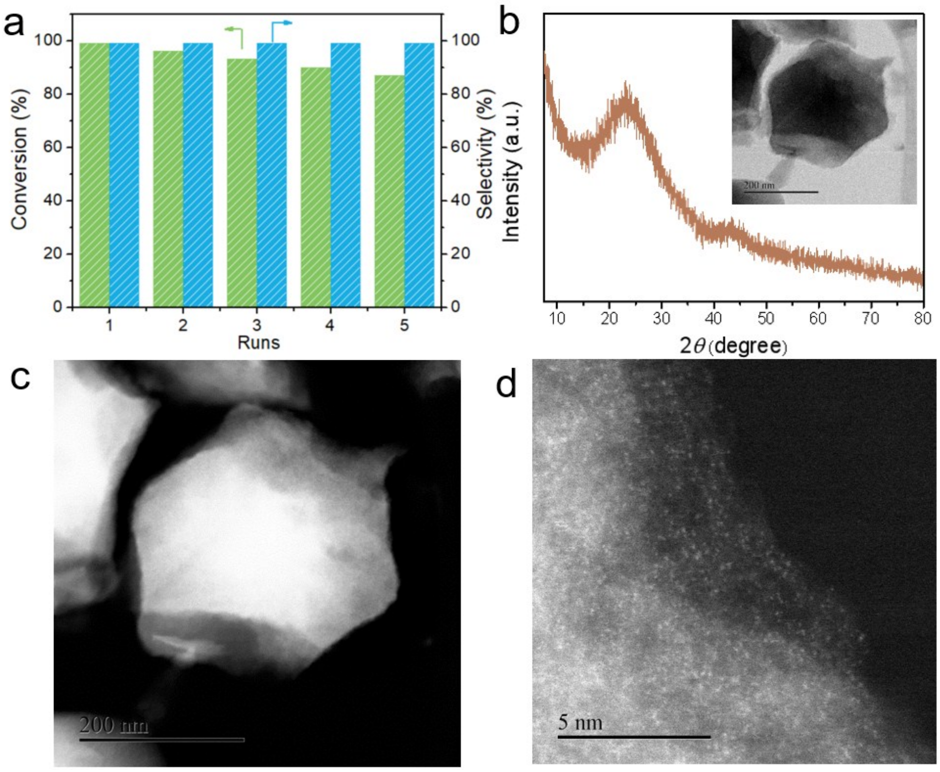
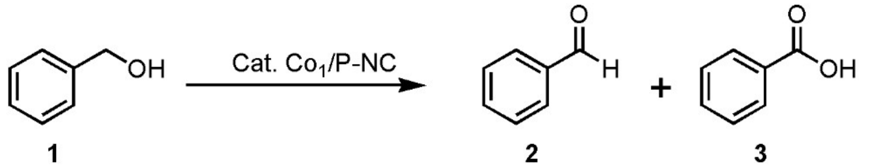


Figure S15. (a) Recyclability of the Co$_1$/P-NC catalyst for oxidation of benzyl alcohol. (b) XRD pattern and TEM image (inset), (c) HAADF-STEM image, (c) AC AADF-STEM image of the used Co$_1$/P-NC catalyst after five reaction cycles.

Table S1. The different reaction conditions of oxidation of benzyl alcohol over Co_1/P-NC catalyst.



Entry[a]	T (°C)	Solvent	Oxidant	Time (h)	Conversion (%)	Selectivity (%)
1	80	Dimethylformamide	H_2O_2	16	67	80
2		Acetonitrile	H_2O_2		28	86
3		Toluene	H_2O_2		74	99
4[b]		Toluene	O_2		48	99
5	100	Toluene	H_2O_2	20	90	99
6	110	Toluene	H_2O_2	12	87	99
7		Toluene	H_2O_2	16	99	99
8		Toluene	H_2O_2	20	99	99
9[c]		Neat	H_2O_2	20	9	99

[a] Reaction conditions: benzyl alcohol (denoted as 1) (0.2 mmol, 1.0 eq), Co_1/P-NC (26 mg, Co: 0.01 eq), H_2O_2 (125 μL) and solvent (2 mL) were mixted and heated at 80-110 °C for 12-24 hours. The yield of the products was determined by GC using tridecane as an internal standard. [b] H_2O_2 (125 μL) was replaced by O_2 (1 bar). [c] The reaction was performed under the same condition with entry 8 except solvent-free.