Supporting Information for

In situ encapsulating cobalt phosphide into quasi-MOF: A high-performance catalyst for hydrolytic dehydrogenation of ammonia borane

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Synthesis of quasi-Co-MOF-74

For the synthesis of quasi-Co-MOF-74, the Co-MOF-74 powders were placed in a porcelain boat and heated at 300 ^{o}C with a heating rate of 5 ^{o}C min^{-1} for 2 h under nitrogen atmosphere.

Synthesis of CoP@C

The Co-MOF-74 powders were placed in a porcelain boat and annealed at 600 ^{o}C for 2 h at a heating rate of 5 ^{o}C min^{-1} under nitrogen atmosphere to obtain Co@C. Afterwards, the prepared Co@C powders were placed in a porcelain boat with $NaH_2PO_2 \cdot H_2O$ ($m_{NaH2PO2 \cdot H2O}$: $m_{Co@C}$ = 10 : 1) at the upstream and annealed at 300 ^{o}C for 2 h with a heating rate of 5 ^{o}C min^{-1} under nitrogen atmosphere.

Synthesis of CoP

The Co-MOF-74 powders were placed in a crucible and annealed at 400 °C for 2 h at a heating rate of 5 °C min^{-1} to obtain Co_3O_4. Afterwards, the prepared Co_3O_4 powders were placed in a porcelain boat with $NaH_2PO_2 \cdot H_2O$ ($m_{NaH2PO2 \cdot H2O}$: m_{Co3O4} = 10 : 1) at the upstream and annealed at 300 °C for 2 h with a heating rate of 5 °C min^{-1} under nitrogen atmosphere.

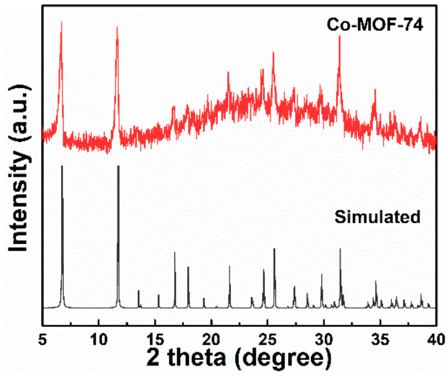

Fig. S1 XRD patterns of simulated and as-prepared Co-MOF-74 (simulated pattern is obtained from the cif document: CCDC 270292).

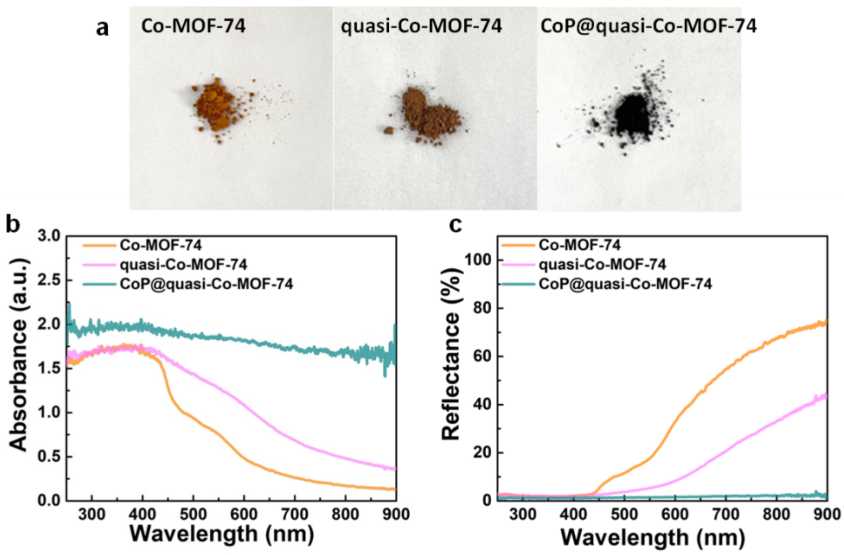

Fig. S2 (a) Photographs of Co-MOF-74, quasi-Co-MOF-74 and CoP@quasi-Co-MOF-74. (b) Diffuse reflectance spectra and (c) Kubelka-Munk transformed diffuse reflectance of Co-MOF-74, quasi-Co-MOF-74 and CoP@quasi-Co-MOF-74.

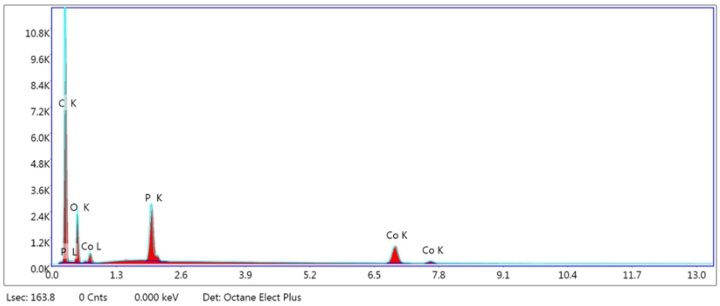

Fig. S3 EDS spectrum of CoP@quasi-Co-MOF-74

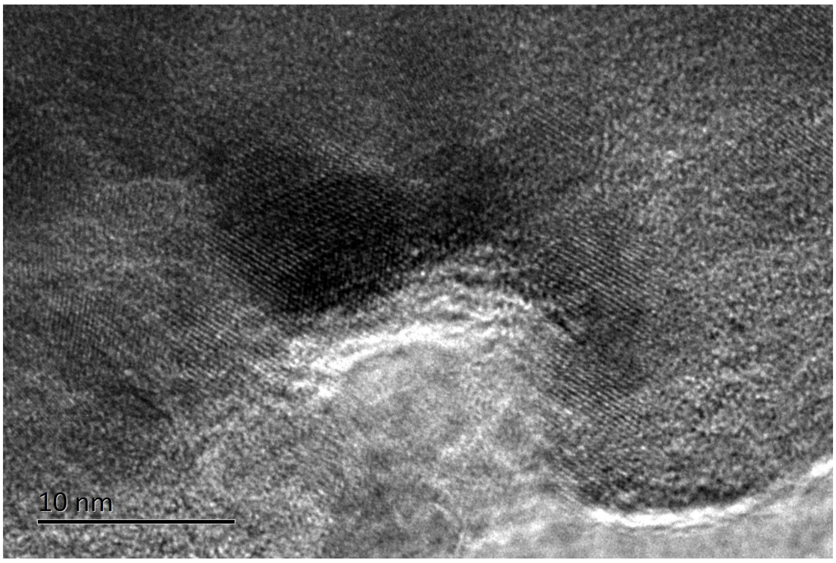

Fig. S4 HRTEM image of CoP@quasi-Co-MOF-74

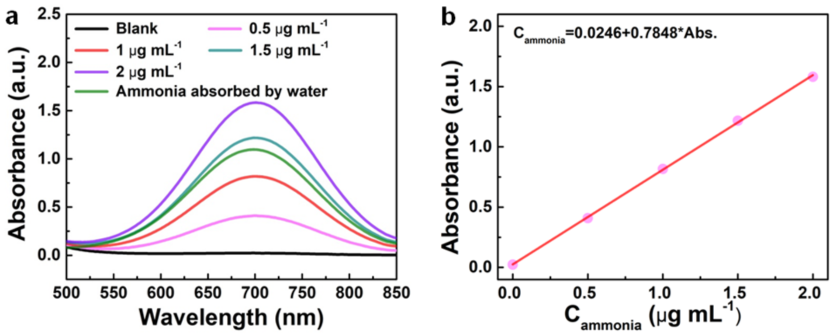

Fig. S5 (a) UV-vis spectra of solutions with different ammonia concentrations. (b) Standard curve for ammonia detection.

Determination of the ammonia

Ammonia is easily soluble while hydrogen is insoluble in water, so ammonia from the mixed gas can be absorbed by water. Ammonia in water was determined by the indophenol blue method.[1] The evolved ammonia was absorbed with 20 mL deionized water. For detection, 0.3 g sodium hydroxide in 9.675 mL water is added to 0.325 mL sodium hypochlorite to obtain solution A, while solution B was prepared by added 0.128 g sodium hydroxide and 0.6404 g $C_7H_5NaO_3$ in 20 mL water. Then, 50 μL solution A, 500 μL solution B and 50 μL of sodium nitrate ferrocyanide solution (10 mg mL^{-1}) were added to 4 mL of absorbed water. After 2 h, solution color was changed from yellow to blue-green, and the presence of ammonia can be detected by UV-visible spectroscopy at a maximum absorption wavelength of 698 nm.

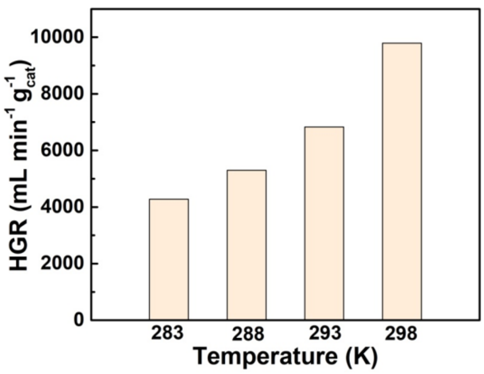

Fig. S6 Effect of reaction temperature on the HGR over CoP@quasi-Co-MOF-74

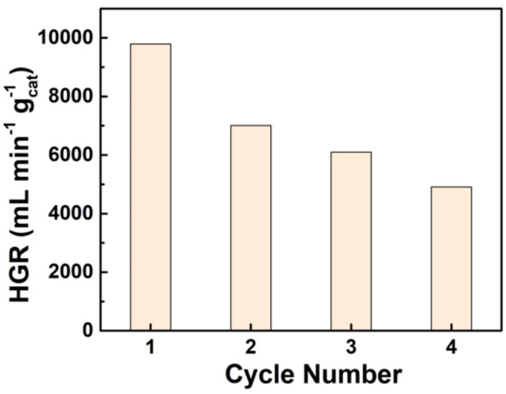

Fig. S7 HGR of CoP@quasi-Co-MOF-74 for catalytic AB hydrolysis for recyclability

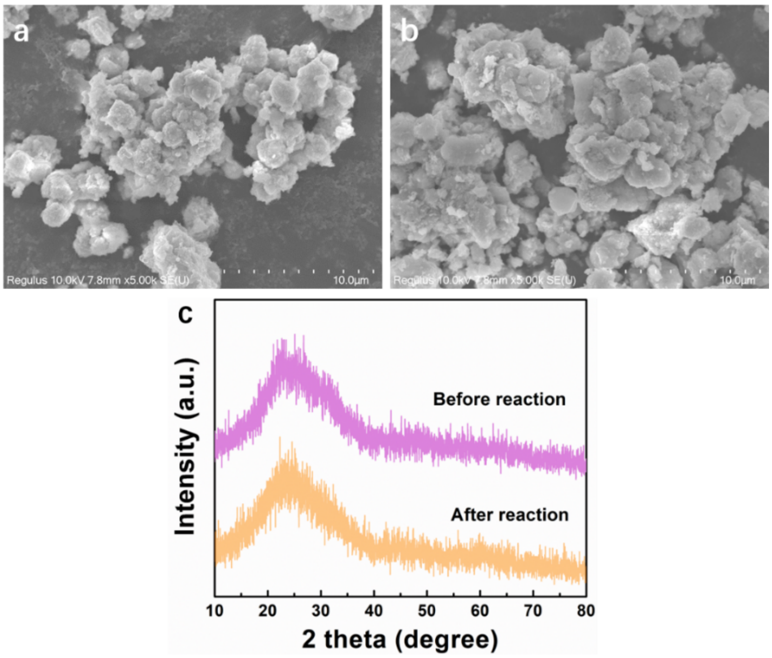

Fig. S8 (a,b) SEM images and (c) XRD pattern of CoP@quasi-Co-MOF-74 after reaction

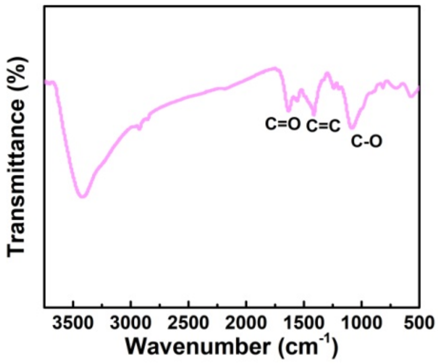

Fig. S9 FTIR spectrum of CoP@quasi-Co-MOF-74 after reaction.

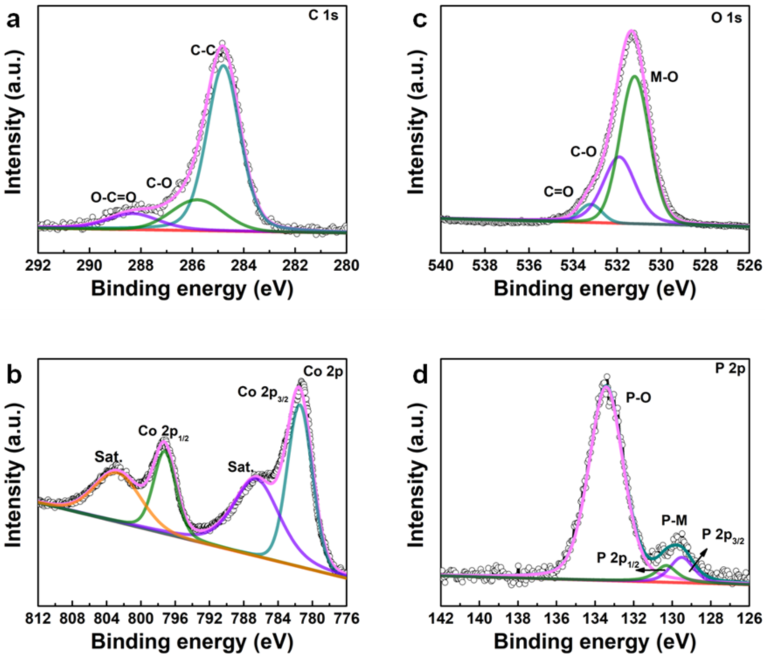

Fig. S10 XPS spectra of CoP@quasi-Co-MOF-74 after reaction: (a) C 1s, (b) O 1s, (c) Co 2p, (d) P 2p.

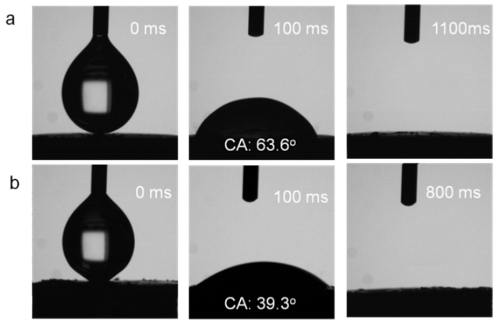

Fig. S11 Water contact angles of (a) Co-MOF-74 and (b) CoP@quasi-Co-MOF-74.

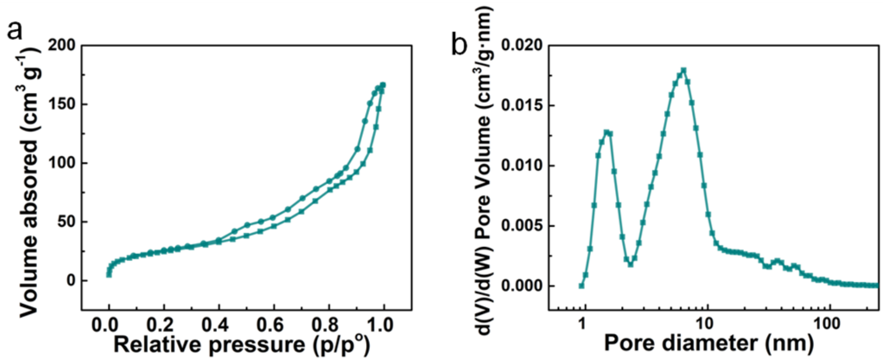

Fig. S12 (a) N_2 adsorption-desorption isotherms and (b) pore-size distribution curve of CoP@quasi-Co-MOF-74.

Table S1 Comparison of HGR for catalytic hydrolysis of AB by different cobalt-based materials

Catalyst	HGR (mL min^{-1} g_{cat}^{-1})	Reference
CoP@quasi-Co-MOF-74	9790	This Work
Co-NC/NF_{600}	1176	2
Co-Ni-B/PAC	1451.2	3
$SCo_{0.43}Cu_{0.57}$	2228.9	4
Co/NPCNW	2638	5
Co-W-B	3327.7	6
Co-Mo-B/CC-F	3916.1	7
CoB	4880	8
Co-B	5500	9
Co-CoO_x@NCS-II	5562	10
Co-CoO_x@GO-II	5813	11
Co-Mo-B/NF	6027.1	11
$Co_{40}Cu_{60}$@S16LC-20	6570	12
Co-Co_3O_4/CDs	6816	13
PEI-GO3D/Co	7680	14

Table S2 Comparison of TOF and E_a for catalytic hydrolysis of AB by different cobalt-based materials

Catalyst	TOF (min^{-1})	E_a (kJ mol^{-1})	Reference
CoP@quasi-Co-MOF-74	55.86	38.22	This Work
Co-NC/NF_{600}	3	64	2
Co/NPCNW	7.3	25.4	5
CoB	4.88	16.2	8
Co-Co_3O_4/CDs	17.93	40	13
Co/HPC	7.3	32.8	15
Co/NC-50	7.6	44.9	16
Co@SiO_2	13.3	42	17

$Co@Co_2P$/N-CNP	18.4	32.1	18
CoP/HPC-500	27.7	42.545	19
CoBP/NGH	32.8	39.42	20
CuO-Co_3O_4	33.4	39.6	21
$Ni_{0.13}Co_{0.87}P$	47.5	41.8	22
$Ni_{0.7}Co_{1.3}P$	58.4	43.2	23
CoP-CoO/NCDS	89.56	41	24

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