Electronic Supplementary Information

Tailoring Three-Dimensional Porous Cobalt Phosphide Templated from Bimetallic Metal-Organic Frameworks as Precious-Metal-Free Catalysts towards Dehydrogenation of Ammonia-Borane

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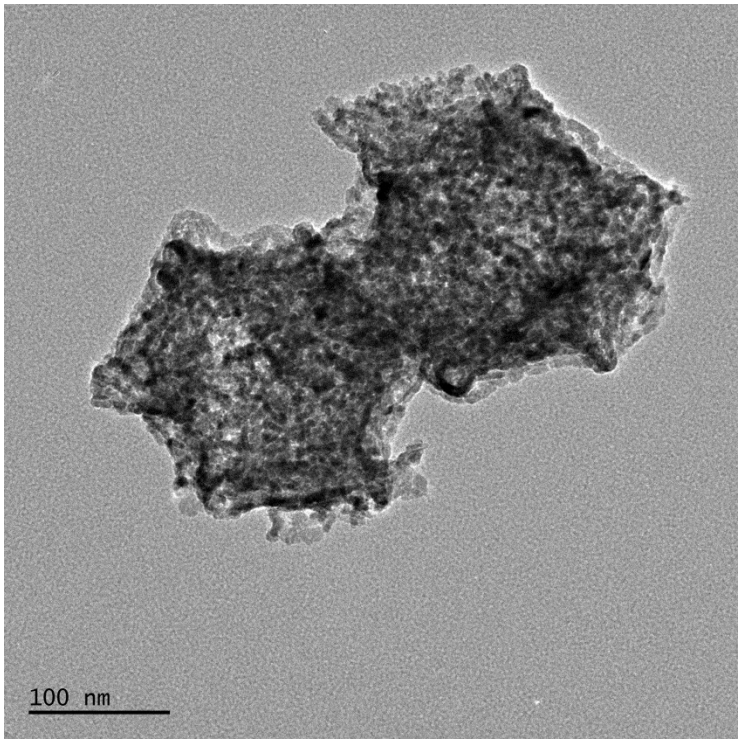

Fig. S1. TEM image of Zn-Co-O@CNF.

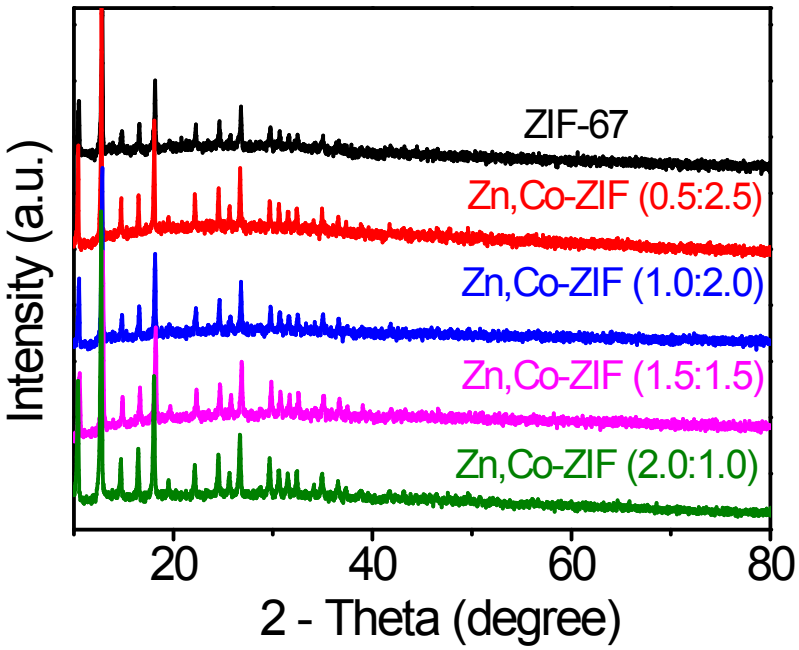

Fig. S2. XRD patterns of ZIF-67 and BZIFs with different Zn:Co molar ratios of 0.5:2.5, 1.0:2.0, 1.5:1.5 and 2.0:1.0.

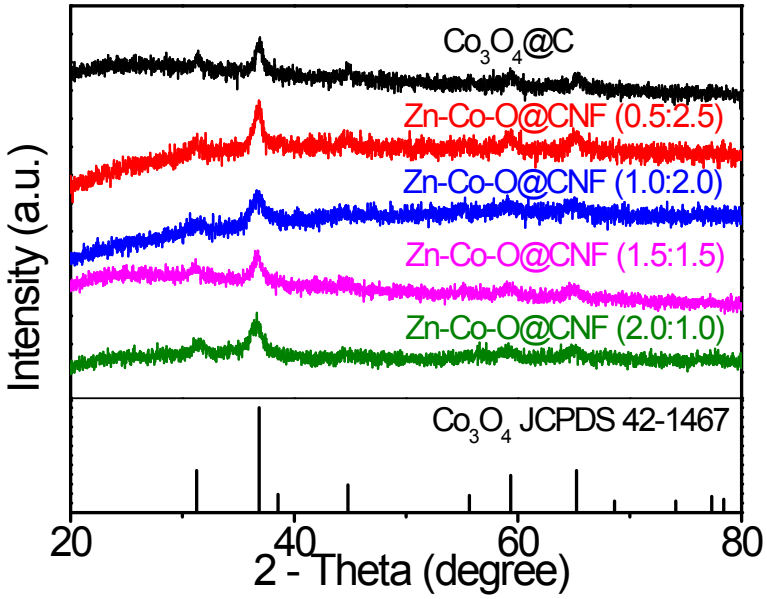

Fig. S3. XRD patterns of Co_3O_4@C and Zn-Co-O@CNF derived from BZIFs with different Zn:Co ratios of 0.5:2.5, 1.0:2.0, 1.5:1.5 and 2.0:1.0.

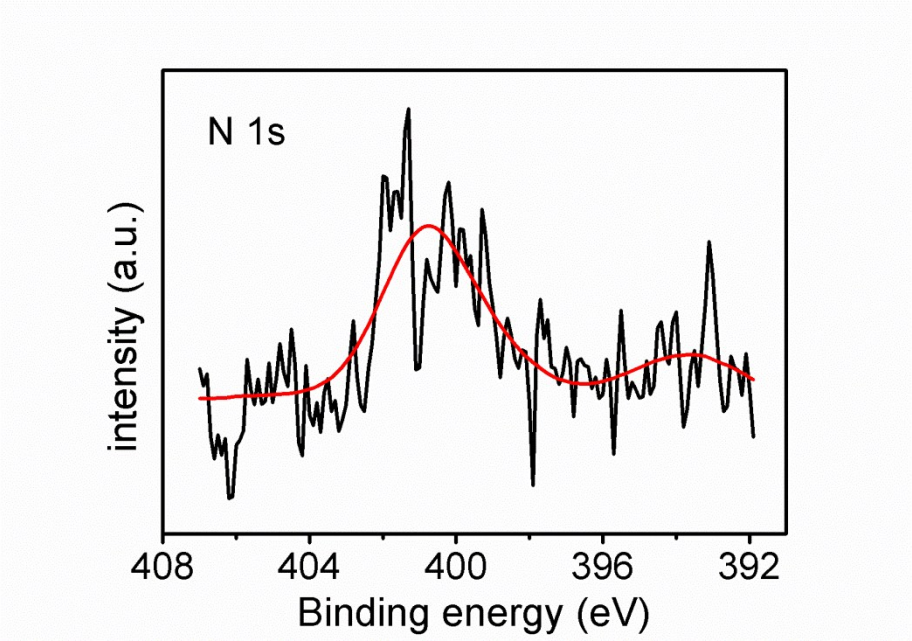

Fig. S4. XPS spectra in the N 1s regions of CoP@CNF.

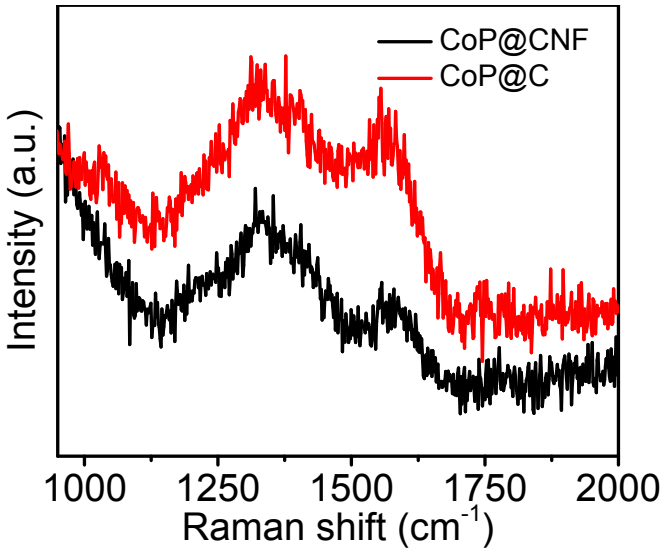

Fig. S5. Raman spectra of CoP@CNF and CoP@C.

The existence of carbon was confirmed by Raman spectroscopy. Two peaks observed at 1349 cm^{-1} and 1581 cm^{-1} belong to the graphite sp^3 carbon (D-band) and disordered sp^2 carbon (G-band), respectively. In addition, the low intensity of peaks indicates the low amount and low crystallinity of carbon in CoP@CNF.

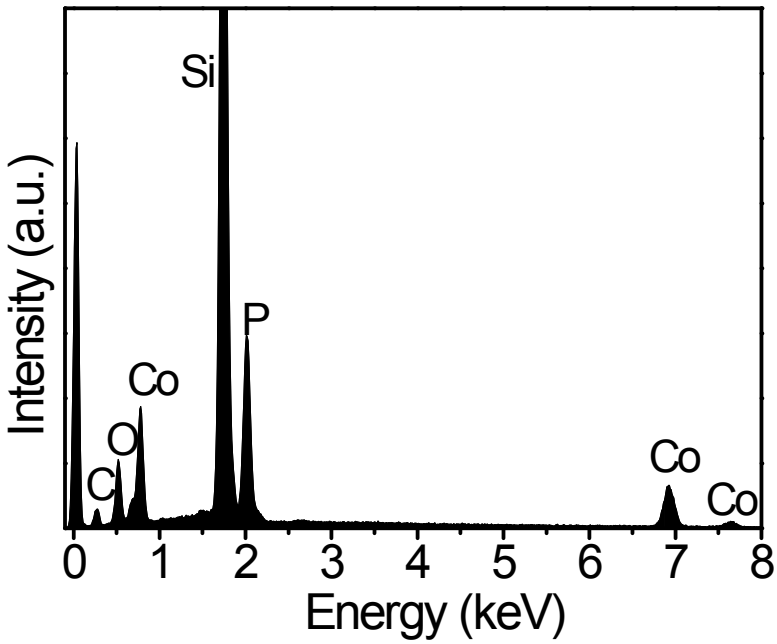

Fig. S6. EDX spectrum of CoP@CNF. The Si peak originates from Si substrate.

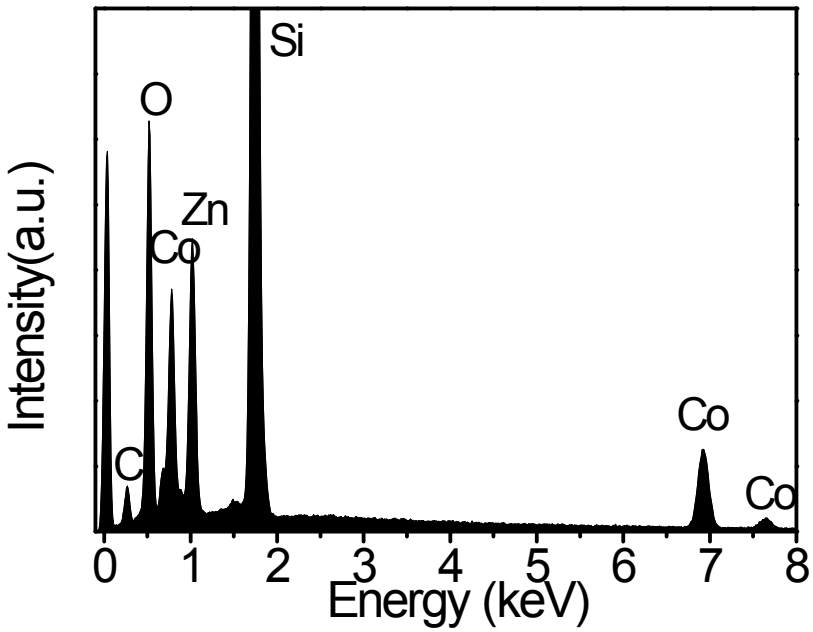

Fig. S7. EDX spectrum of Zn-Co-O@CNF. The Si peak originates from Si substrate.

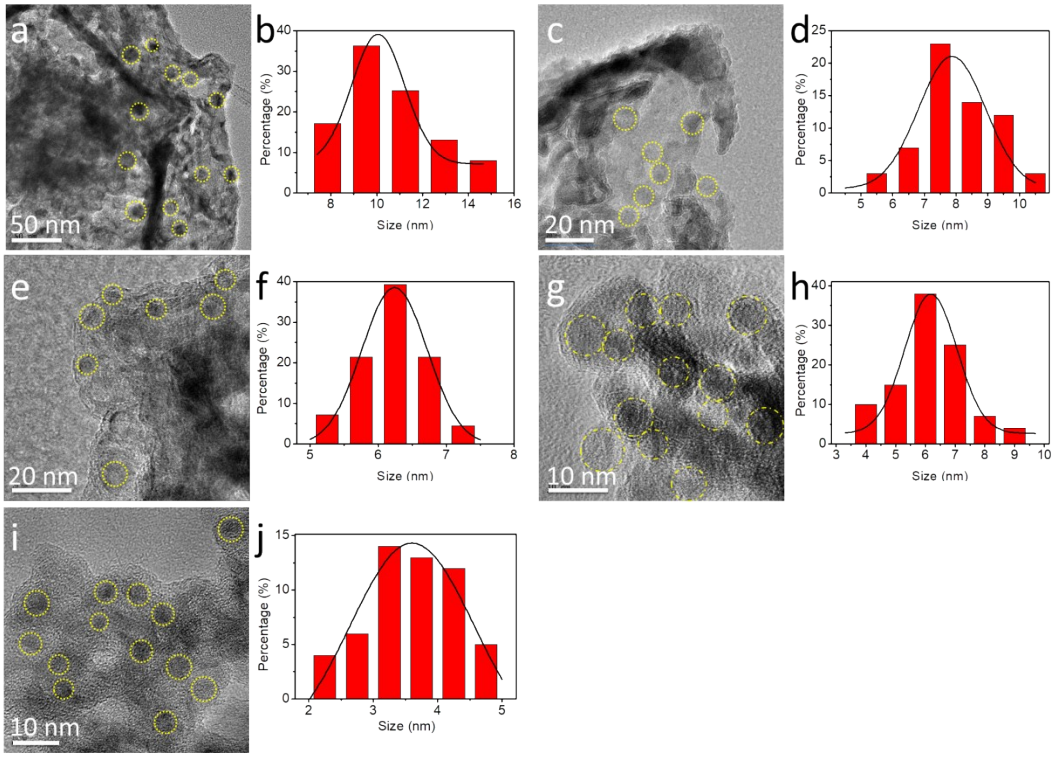

Fig. S8. (a,c,e,g,i) TEM images and (b,d,f,h,j) corresponding to the size distributions of CoP@C, and as-prepared CoP@CNF with different Zn:Co molar ratios of 0.5:2.5, 1.0:2.0, 1.5:1.5 and 2.0:1.0.

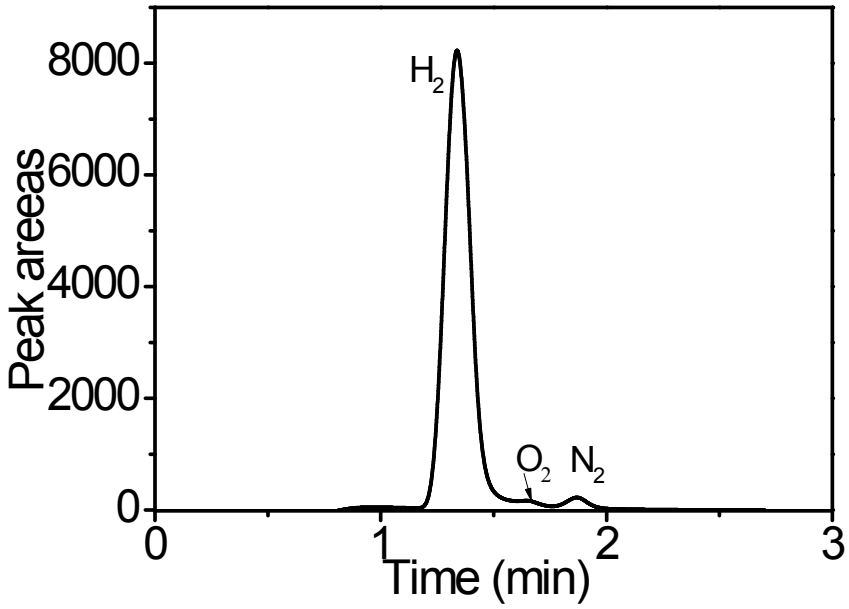

Fig. S9. Recorded peak area of iso-volumetric gases corresponding to labeled H_2 produced in reaction systems.

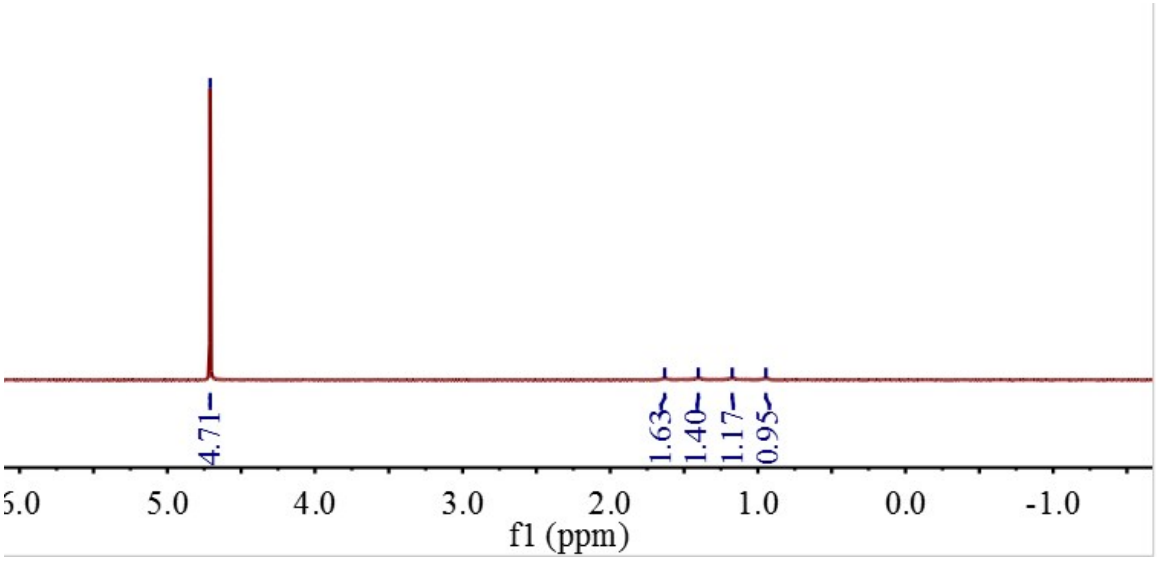

Fig. S10. ^1H NMR spectrum of a NH_3BH_3 solution in D_2O before reaction at 298 K.

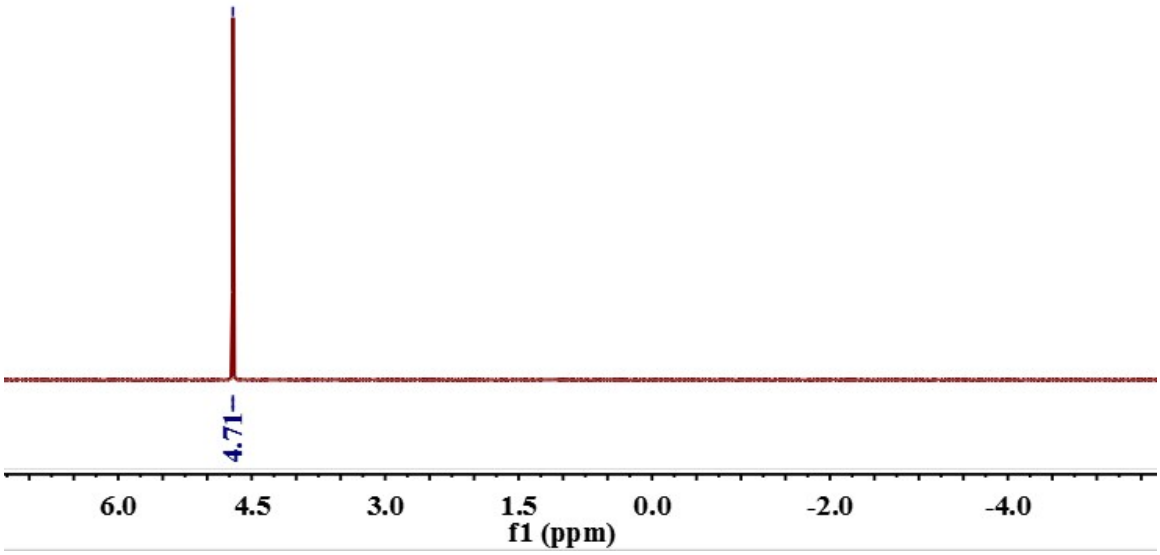

Fig. S11. ^{1}H NMR spectrum of a NH_3BH_3 solution in D_2O after reaction at 298 K.

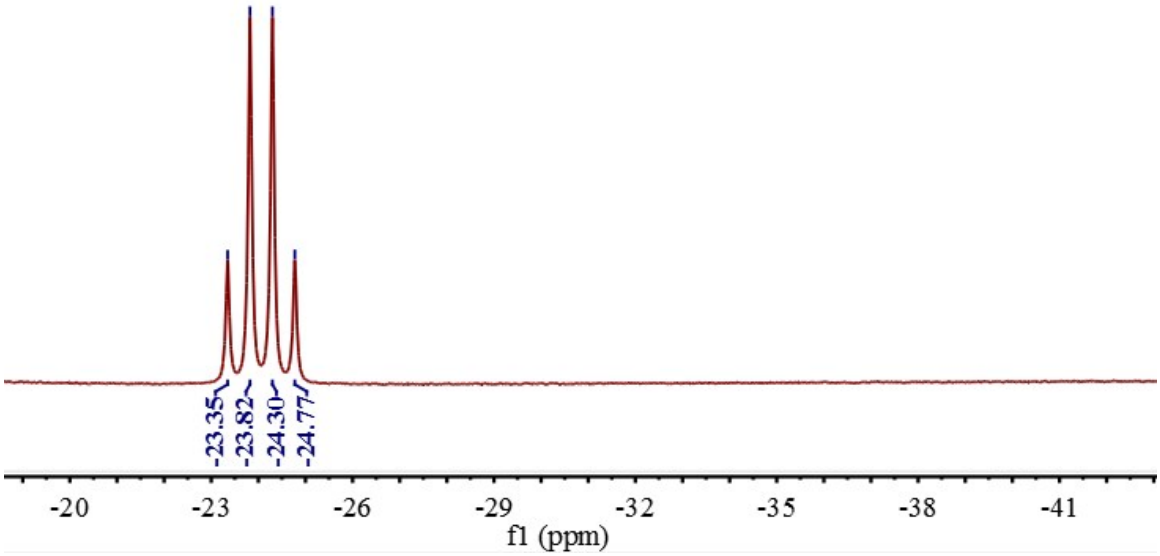

Fig. S12. ^{11}B NMR spectrum of a NH_3BH_3 solution in D_2O before reaction at 298 K.

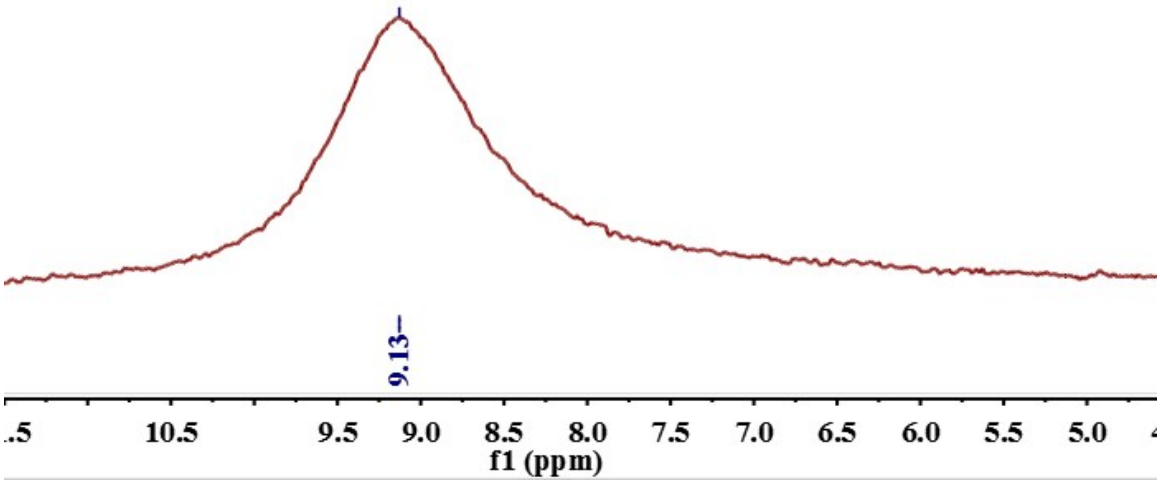

Fig. S13. ^{11}B NMR spectrum of a NH_3BH_3 solution in D_2O after reaction at 298 K.

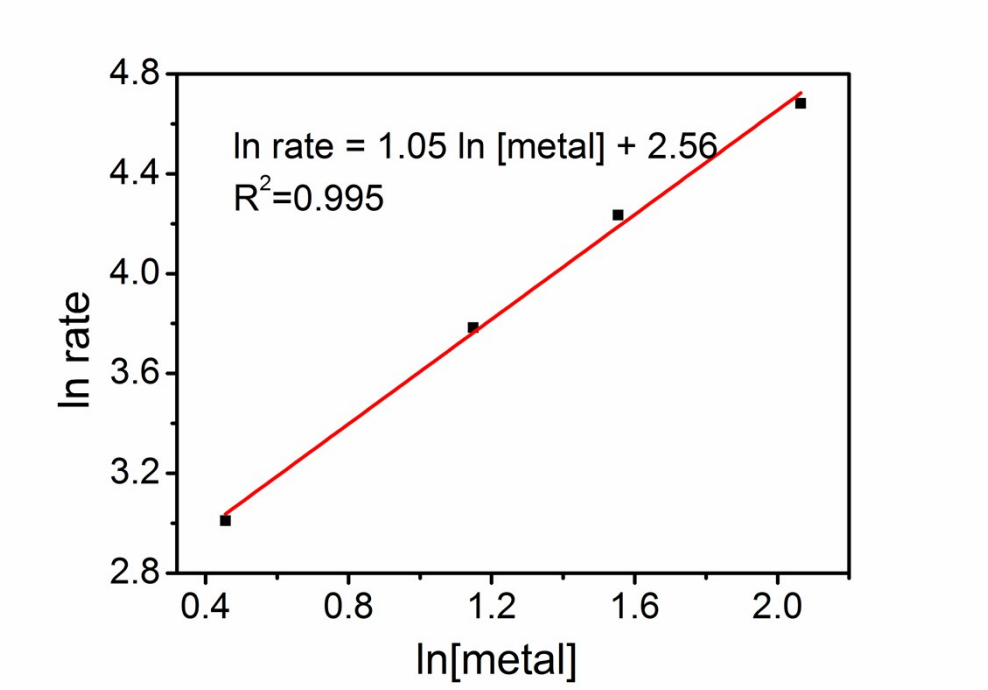

Fig. S14. Logarithmic plot of H_2 generation rate versus [metal].

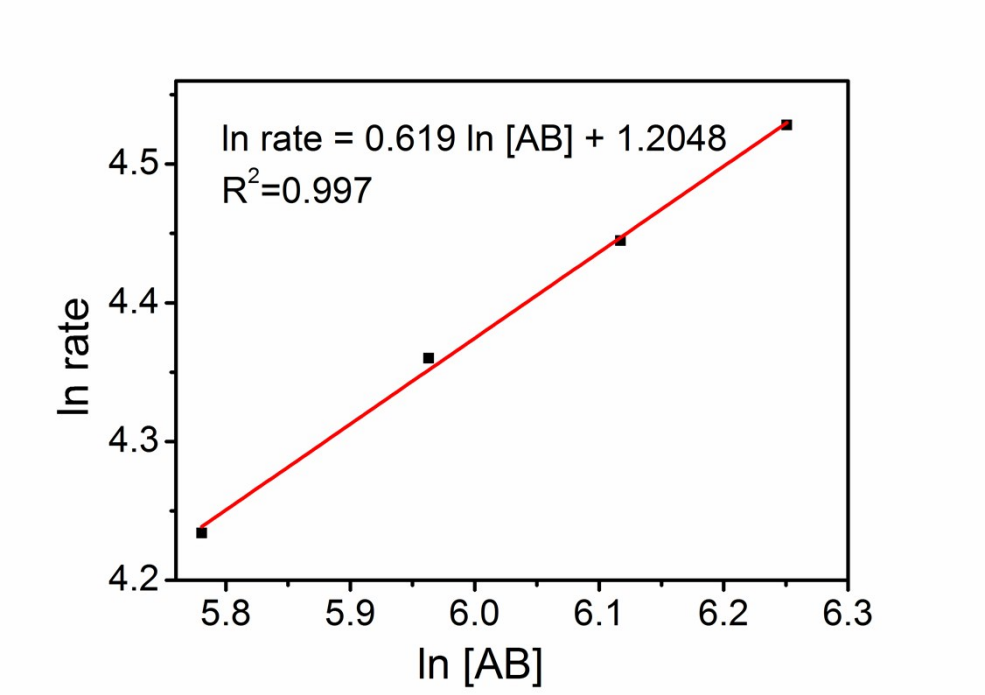

Fig. S15. Logarithmic plot of H_2 generation rate versus [AB].

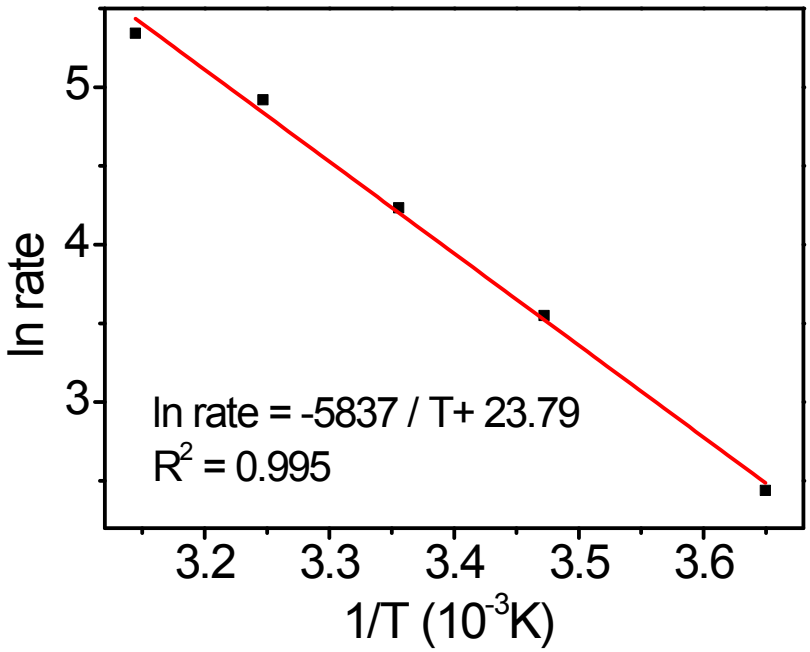

Fig. S16. Arrhenius plot of ln rate versus 1/T. The activation energy is caculated to be 48.5 kJ mol^{-1} for CoP@CNF (1.5:1.5) sample in the catalytic hydrolysis of AB.

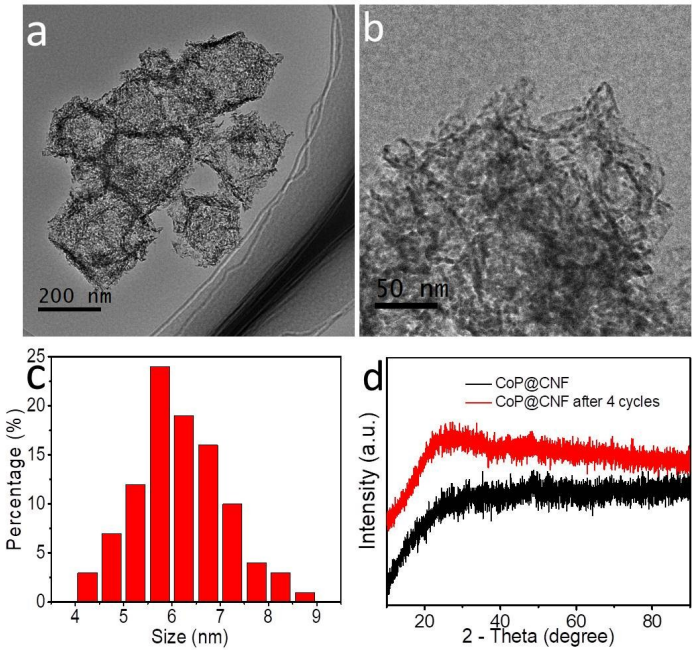

Fig. S17. (a, b) TEM images of CoP@CNF after 4 cycles for catalytic reactions. (c) The size distribution of CoP nanoparticles in (b). (d) XRD patterns of CoP@CNF before and after stability test.

Table S1. Surface areas of metal phosphides derived from MOFs reported in literatures.

Sample	MOF precusor	Surface areas ($m^2 g^{-1}$)	Reference
CoP@CNF	Zn/Co-ZIF	145.3	This work
CoP polyhedron	ZIF-67	46.9	1
$Co_{0.38}Fe_{0.62}P$	PBA	43.9	2
Ni_5P_4-Ni_2P@C nanoplates	Ni-Ni PBA	35.0	3
FeP nanocubes	PB	39.6	4
CoP concave polyhedrons	ZIF-67	29.4	5
CoP/rGO-400	ZIF-67	40.0	6
CoP nanosheet	ZIF-67	94.5	7
CoP@BCN	ZIF-67	146.0	8
Co4Ni1P NTs	MOF-74	55.6	9
CoP@GC	ZIF-67	92.0	10

Table S2. ICP-OES results of CoP@C and CoP @CNF with different Zn:Co molar ratios.

Samples	CoP@C	CoP@CNF (0.5:1.5)	CoP@CNF (1.0:2.0)	CoP@CNF (1.5:1.5)	CoP@CNF (2.0:1.0)
Mass ratio(%) of CoP	91.13	85.39	83.98	78.20	75.28

Table S3. Elemental contents of CoP@CNF (1.5: 1.5) obtained by XPS.

Elements	C	O	Co	P	N
Content (wt%)	8.79	22.01	39.33	29.11	0.76[a]

[a] The data is obtained by EDX.

Table S4. Activities of catalysts in H_2 generation from hydrolysis of NH_3BH_3 reported in literatures.

Catalyst	TOF [mol(H_2) mol (catalyst)$^{-1}$ min^{-1}]	T (K)	Reference
CoP@CNF	165.5[a]	298	This work
CoP	72.2[a]	298	11
$Cu_xCo_{1-x}O$-GO	70.7	298	12
CuO-NiO	60	298	13
$Cu_{0.5}Ni_{0.5}$/CMK-1	54.8	298	14
Ni_2P	40.4	298	15
Co/CNT	42.3	298	16
$Ni_{0.9}Mo_{0.1}$/graphene	66.7	298	17
PEI-GO/Co	39.9	298	18
Ni nanoparticles	8.8	298	19
RGO/Pd	6.25	298	20
Co NPs(in situ)	49.8	298	21
Co/graphene	13.8	298	22
Co@N-C-700	5.6	298	23
Ni/ZIF-8	14.2	298	24
Ni/CNT	26.2	298	25
Ni@MCS-30	30.7	298	26
$Cu_{0.49}Co_{0.51}$/C	28.7	298	27
Ni NPs@3D-(N)GFs	41.7	298	28
Cu NPs@SCF	40.0	298	29

[a]The reaction was performed in alkaline ammonia-borane solution.

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