COMMUNICATION

Supporting Information

Ultrasmall cobalt nanoparticles supported on nitrogen-doped porous carbon nanowires for hydrogen evolution from ammonia borane

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Experimental Section

Synthesis

Synthesis of Co/NPCNW: $Co(NO_3)_2 \cdot 6H_2O$ (0.873 g, 3 mmol)), H_3BTC (H_3BTC=1,3,5-benzenetricarboxylic acid, 0.633 g, 3 mmol), and 4,4'-bipy (4,4'-bipy=4,4'-bipyridine, 0.576 g, 3 mmol) were dissolved in 60 mL DMF (DMF=N,N-dimethylformamide), then sealed in 100 mL Teflon-lined autoclave and kept at 353 K for 72 h prepared by a solvothermal synthesis route. When cooled down to room temperature, the product was washed thoroughly with DMF for three times during the vacuum filtration. At last, calcine the above dried sample in a flow of ultrapure Ar for 2 h at 700 °C with a heating rate of 5 °C min^{-1}.

Synthesis of Co/C: H_3BTC (0.422 g, 2 mmol) and $Co(Ac)_2 \cdot 6H_2O$ (0.584 g, 2 mmol) were dissolved in 60 mL deionized water, then sealed in 100 mL Teflon-lined autoclave and kept at 413 K for 48 h. When cooled down to room temperature, the product was washed thoroughly with deionized water for three times during the vacuum filtration. At last, calcine the above dried sample in a flow of ultrapure Ar for 2 h at 600 °C with the heating rate of 5 °C min^{-1}.

Characterization

The as-synthesized catalysts were characterized by powder X-ray diffraction (XRD, Rigaku MiniFlex600, Cu Kα radiation), scanning electron microscopy (SEM, JEOL JSM 7500F) and transmission electron microscopy (TEM, Philips Tecnai F20). The specific surface area was tested by nitrogen adsorption-desorption measurement (BELSORP-Mini) at 77 K. The X-ray photoelectron spectra (XPS) was conducted on an PHI 5000VersaProbe instrument. FTIR spectra was collected by using a FTIR-650 spectrometer at a resolution of 4 cm^{-1} at room temperature.

Hydrogen Generation Measurements

The hydrogen generation experiments were carried out at 25 °C using the typical water displacement method. In general, a certain amount of catalyst (10 mg) was placed in a one-neck round-bottom flask, adding 8 mL deionized water and then stirring for a few minutes. An inverted, water-filled gas burette in a water-filled vessel was to monitor the evolved H_2 volume. The hydrolysis reaction was started when 40 mg AB power was added to the flask. The generated gas from AB hydrolysis was extracted and injected into gas chromatography (Bruker SCION 456GC) to test the purity of H_2. The hydrolysis reactions of AB were also performed at 35 °C, 45 °C, 55 °C. When the hydrolytic dehydrogeneration was completed, the catalysts were magnetically attached to the botton of the flask. Remove the supernatant liquid and add 40 mg AB power to run the reusability test under the same condition at 25 °C. Considering the magnetic property of the cobalt nanoparticles, the catalysts attaching to the magneton could be washed away by deionized water and be collected for the reproducibility test. Then the mixed solution was filtered, and the obtained powder was washed with deionized water and absolute ethanol and dried in a vacuum oven at 60 °C for 10 h. Then the dried sample was use for next hydrolysis system.

Leaching test

The experimental protocol was put the mixture of Co/NPCNW and ultrapure water (a solid-liquid ratio of 1:10 (kg L^{-1})) into pyrex flask. Then shake the mixture for 24 h on flip type oscillator with a speed of 30 r min^{-1}. The undissolved reside was seprated by filtration using a membrane filter of pore size 0.45 μm, which had been prewashed with ultrapure water. Finally, the concentration of extracted Co was measured by ICP test.

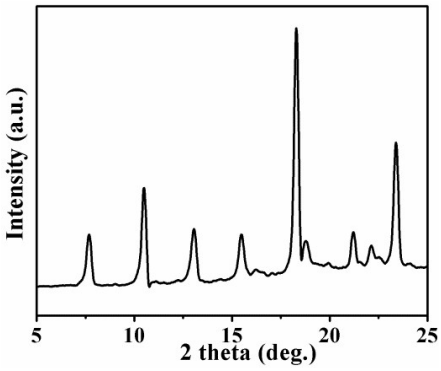

Figure S1. XRD pattern of the as-prepared Co-MOF.

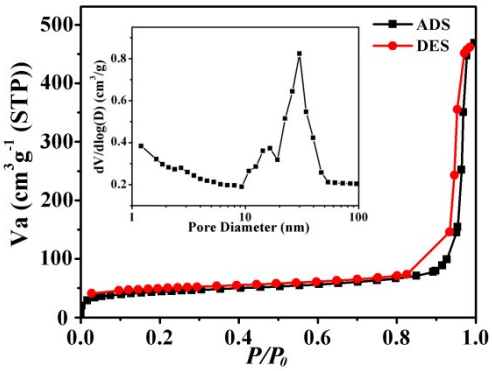

Figure S2. N_2 adsorption-desorption isotherm of the as-prepared Co-MOF (inset is the pore-size distribution of Co-MOF).

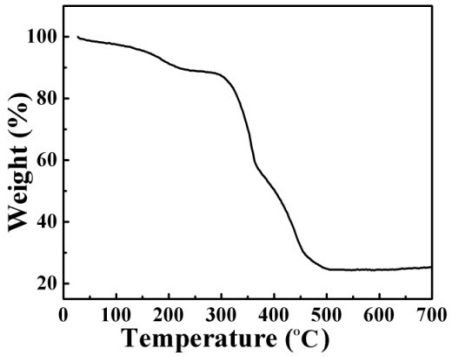

Figure S3. TG curve of Co/NPCNW between 0 and 700 °C measured with a heating rate of 5 °C min^{-1} under Ar atmosphere.

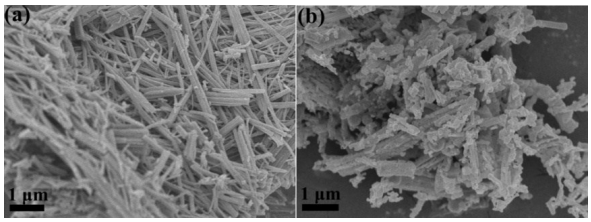

Figure S4. SEM images of the calcined Co-MOF with the calcinaiton temperature at 700 °C (a) and 800 °C (b) for 2 h.

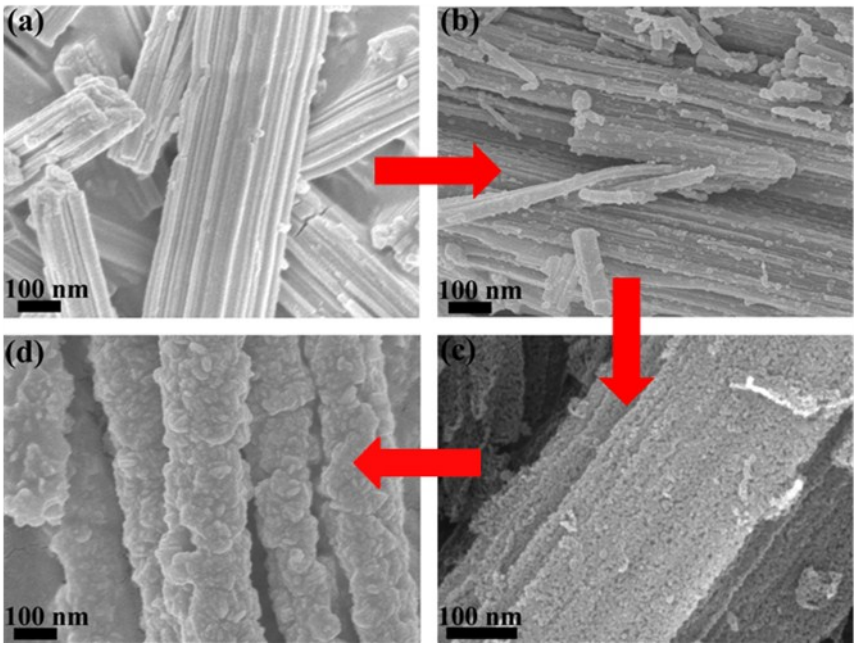

Figure S5. SEM images of the Co-MOF (a) and the calcined samples for 1 h (b), 2 h (c), 3 h (d) at 700 °C.

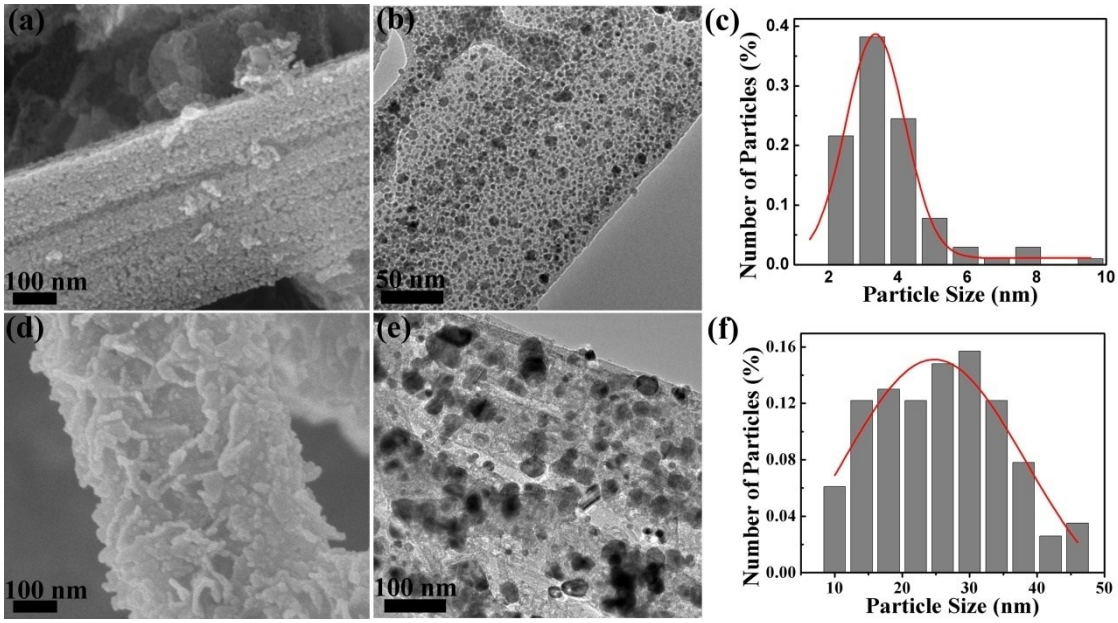

Figure S6. SEM and TEM images of the calcined Co-MOF for 2 h (a, b) and 3 h (d, e) at 700 °C and the corresponding size distribution of cobalt nanoparticles (e, 2 h; f, 3 h).

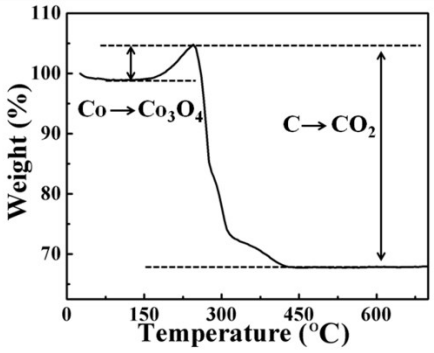

Figure S7. TG curve of Co/NPCNW between 0 and 700 °C measured with a heating rate of 5 °C min^{-1} under air atmosphere.

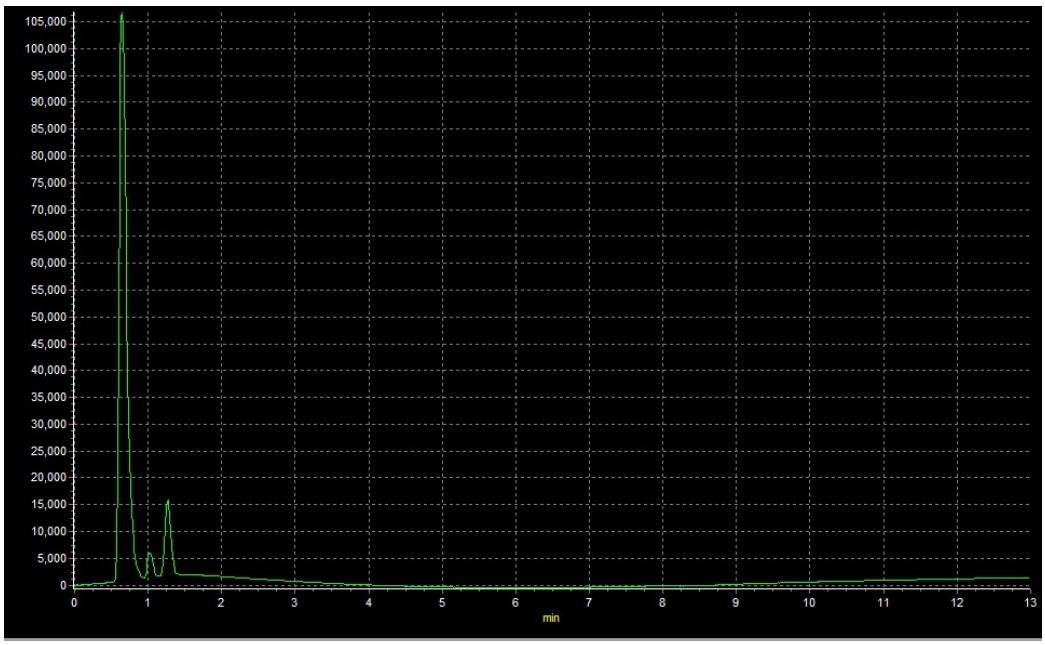

Figure S8. Gas chromatography (GC) of the generated gas from AB hydrolysis.

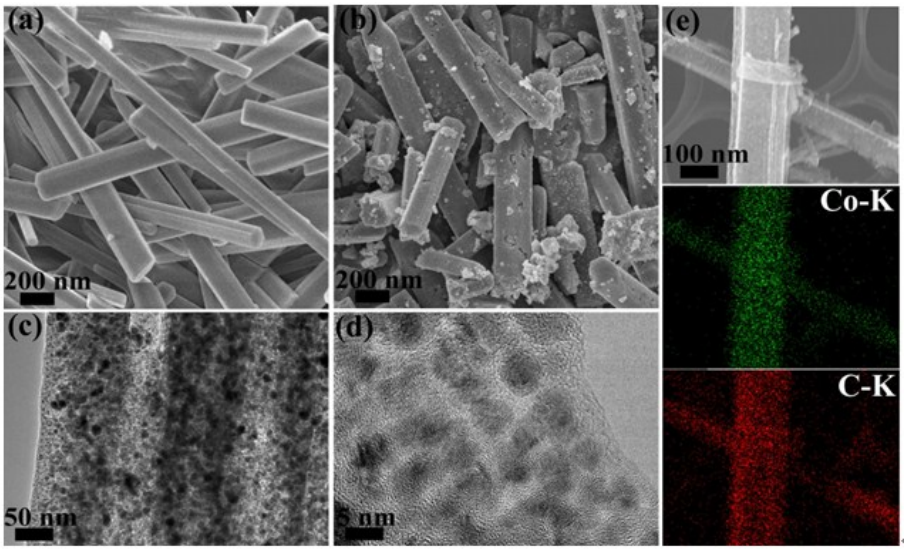

Figure S9. SEM images of Co-MOF (the precursor of Co/C) (a) and Co/C (b); TEM (c), HRTEM images (d), and SEM mapping (e) of Co/C.

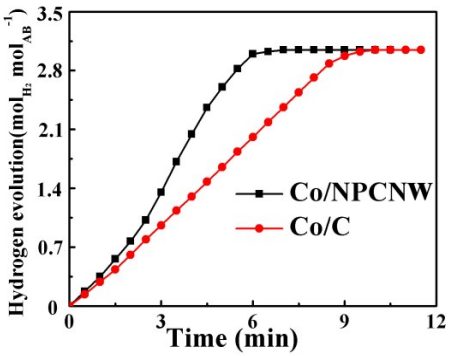

Figure S10. Plot of equivalent H_2 per mole of AB vs. time from AB solution (0.5 wt%, 8 mL) catalyzed by 10 mg Co/C and Co/NPCNW at room temperature.

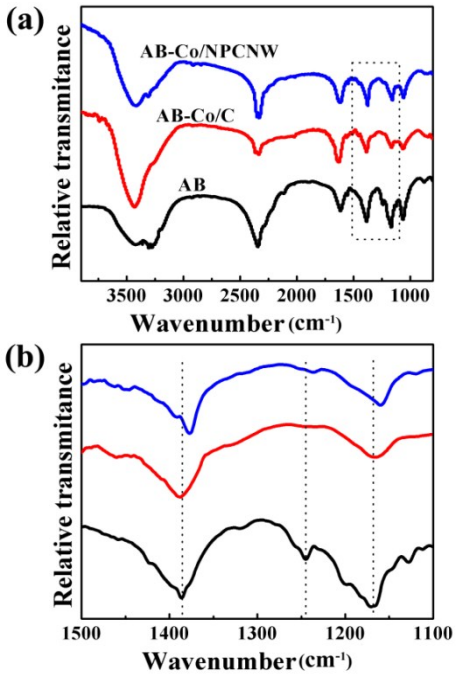

Figure S11. FTIR spectra of (a) AB-Co/NPCNW (blue), Co/C (red), AB (black), (b) Magnified picture of the rectangular area marked in (a).

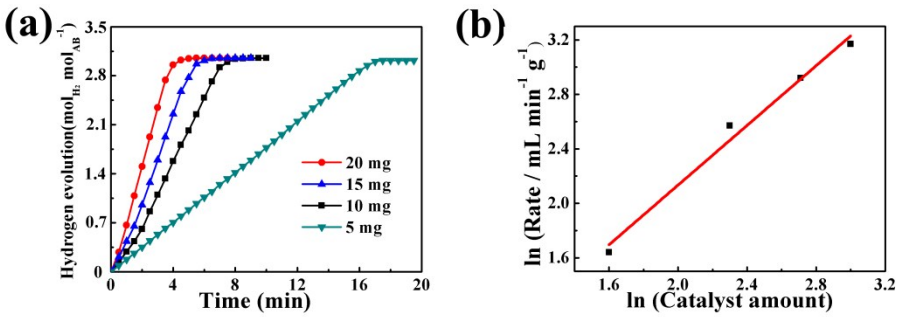

Figure S12. (a) Plot of equivalent H_2 per mole of AB vs. time from AB solution (0.5 wt%, 8 mL) catalyzed by different amount of Co/NPCNW (5, 10, 15, 20 mg) at room temperature, (b) Plot of hydrogen generation rate vs. catalyst amount in logarithmic scale.

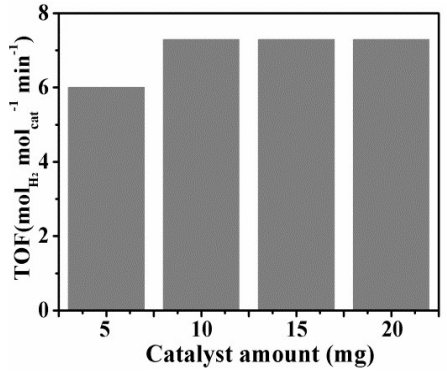

Figure S13. Plot of of TOF vs the amount of catalyst Co/NPCNW.

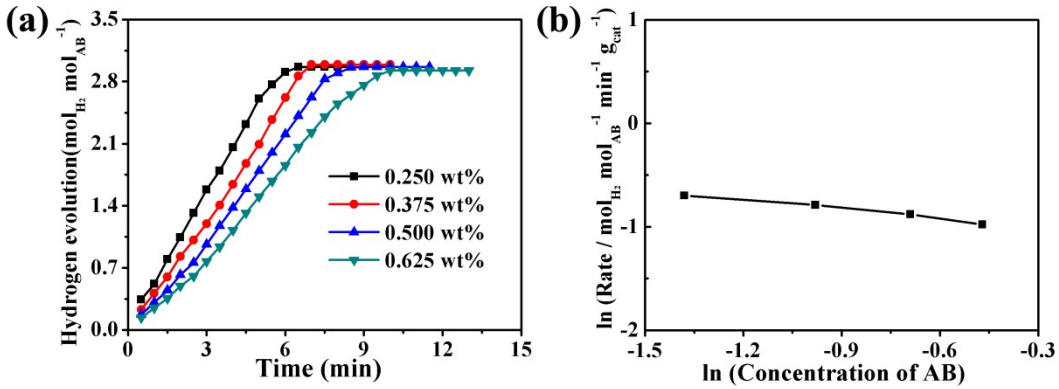

Figure S14. (a) Plot of equivalent H_2 per mole of AB vs. time from AB solution catalyzed by 10 mg Co/NPCNW at different AB concentration (0.250, 0.375, 0.500, 0.625 wt%) at room temperature, (b) Plot of hydrogen generation rate vs. AB concentration in logarithmic scale.

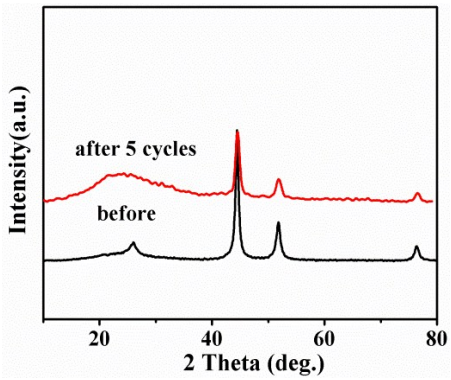

Figure S15. XRD patterns of the Co/NPCNW before and after 5 cycles.

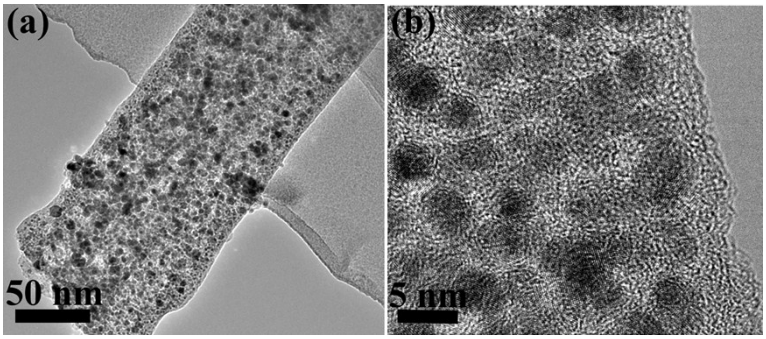

Figure S16. TEM (a) and HRTEM (b) images of the Co/NPCNW after 5 cycles.

Table S1 Hydrogen generation (HG) from the hydrolysis of AB catalyzed by Co-based catalysts

Catalyst	TOF (mol_{H_2} mol_{cat}^{-1} min^{-1})	Ea (kJ mol^{-1})	Cycle number-retained catalytic activity (%)	Ref.
Co/NPCNW	**7.29**	**25.4**	**10-94.6**	**This work**
Co	0.88	_	_	1
PEI-GO/Co	39.9	28.5	5-65.6	2
Co/graphene	13.8	32.75	5-60	3
Co/hydroxyapatite	4.54	52	5-81	4
Intrazeolite cobalt (0) nanoclusters	5.32	56	5-69	5
AuCo alloy	6.0	_	_	6
PSMA-Co	25.7	34	_	7
Silica-embedded cobalt(0)	_	4 2	5-74	8
Co film	_	_	6-60	9
Ti-supported Co film	1.7	28.0	_	10
Co-SAG	7.17	46.4	_	11
10 wt% Co/ γ −Al2O3	2.08	62	_	12

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