

Supporting Information

Synergistic catalytic hydrolysis of ammonia borane to hydrogen release over AgCo@CN

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Experimental

Materials and Reagents

Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR), 2-methylimidazole (AR), silver nitrate (AgNO_3 , AR), and ammonia borane (AB), were purchased from Aladdin Bio-Chem Technology Co., Ltd (China). All chemicals were used without further purification.

Characterization

The morphology and structure of the samples were characterized using transmission electron microscopy (TEM) on a JEOL JEM-2100 FEGTEM. The morphology and distribution of element of the catalysts were tested by scanning electron microscopy (SEM, Sigma 500 field emission scanning electron microscope). Powder X-ray diffraction (XRD) was performed on Rigaku D/Max-2400X with Cu K α radiation. X-ray photoelectron spectroscopy (XPS) spectra were obtained from an ESCALABMKLL X-ray photoelectron spectrometer using an Al K α source. The concentration of metals in the catalyst was measured via inductively coupled plasma optical emission spectrometry (ICP-OES, 213DFG/ICPE-9820 Shimadzu multitype ICP emission spectrometer).

Preparation of Co@CN

In a typical procedure, 3 mL $\text{Co}(\text{NO}_3)_2$ solution (0.15 g mL^{-1}) was dispersed into 20 mL 2-methyl imidazole solution (0.275 g mL^{-1}). After continuous stirring for 6 h and aging for 24 h, the product was collected by centrifugation and then dried at 333 K for 8 h

under vacuum. The obtained solid was calcinated at 873 K for 5 h in Ar, with a heating rate of 5 K min⁻¹.

Catalytic procedure

Typically, the as-prepared Co@CN (10 mg) was added in a 25 mL two-necked flask, and then 4 mL solution containing a certain volume of AgNO₃ solution (0.1 M) and deionized water was added. The mixture was stirred in the dark for 16 h at room temperature. Afterward, 1 mL AB aqueous solution (1 M) was injected into the flask. Volume of hydrogen production was measured by a water displacement method. During the reaction, the reaction temperature was controlled by a water bath. Effect of Ag concentration on catalytic AB hydrolysis over AgCo@CN was investigated by changing the concentrations of Ag precursor (i.e., 0.27, 0.54, 1.05, 2.08 mM) while keeping other conditions unchanged. The hydrolysis reaction of different dosages of AB (i.e., 100, 200, 300, 400 mM) were carried out while keeping other conditions unchanged. Moreover, the AB hydrolysis was conducted at different reaction temperatures (i.e., 293, 298, 303, 308 K) to explore the reaction thermodynamics and calculate the activation energy (E_a).

The reusability experiments of AgCo@CN were performed under the reaction conditions of 1 mL AB (1 M) and 4 mL water at 298 K. When the previous cycle was finished, another 1 mL fresh AB solution was added to begin the next reaction. After the reusability test, the black solid was collected for characterization.

Calculation

The TOF value was determined based on the reported literature using the eq. S1.

$$TOF = \frac{P_{atm} V_{H_2} / RT}{n_{Ag} t} \quad (S1)$$

where P_{atm} is the atmospheric pressure (101325 Pa), V_{H_2} is the volume of generated hydrogen when conversion rate of 50%, R represents the ideal gas constant (8.314 J mol⁻¹·K⁻¹), T is the reaction temperature (K), n_{Ag} is the total mole number of Ag atoms in catalyst, and t is the reaction time when conversion rate of 50%.

The E_a was determined based on the reported literature using the eq. S2.

$$\ln k = \ln A - E_a / RT \quad (S2)$$

where K is the estimated rate constant, A is the frequency factor, R and T represent the ideal gas constant and temperature respectively.

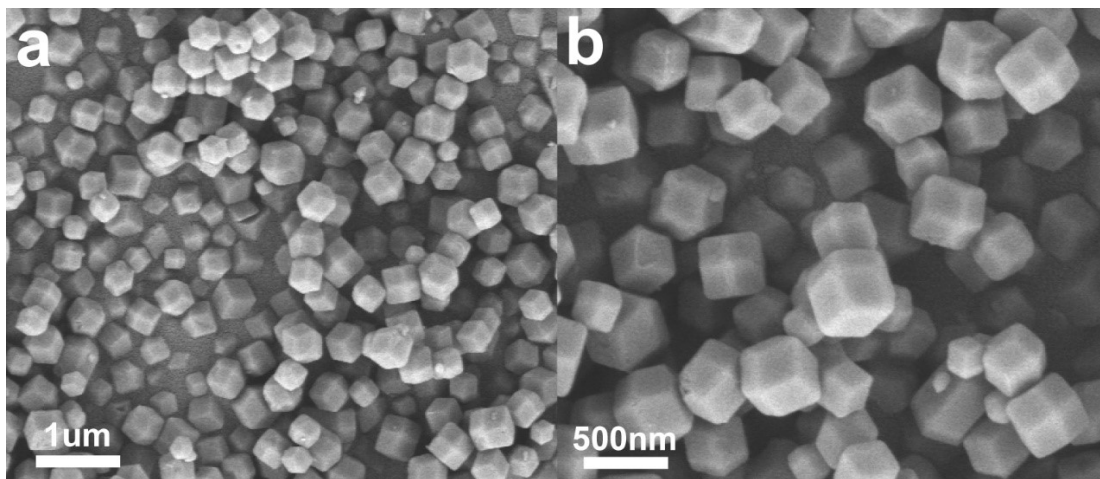


Fig. S1. The SEM images of ZIF-67.

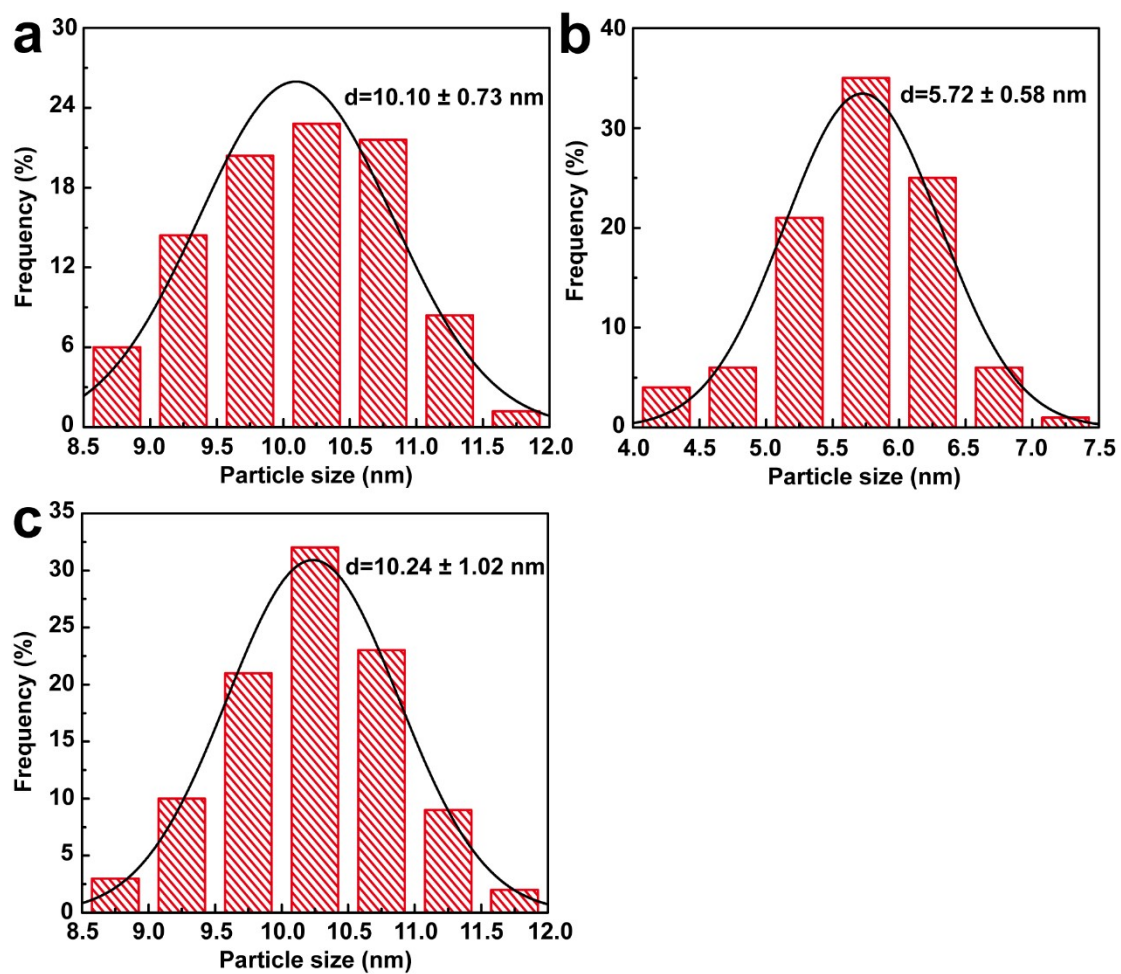


Fig. S2. The corresponding particle size distribution diagrams of (a) Co and (b) Ag NPs of the AgCo@CN catalyst, and (c) Co NPs of Co@CN.

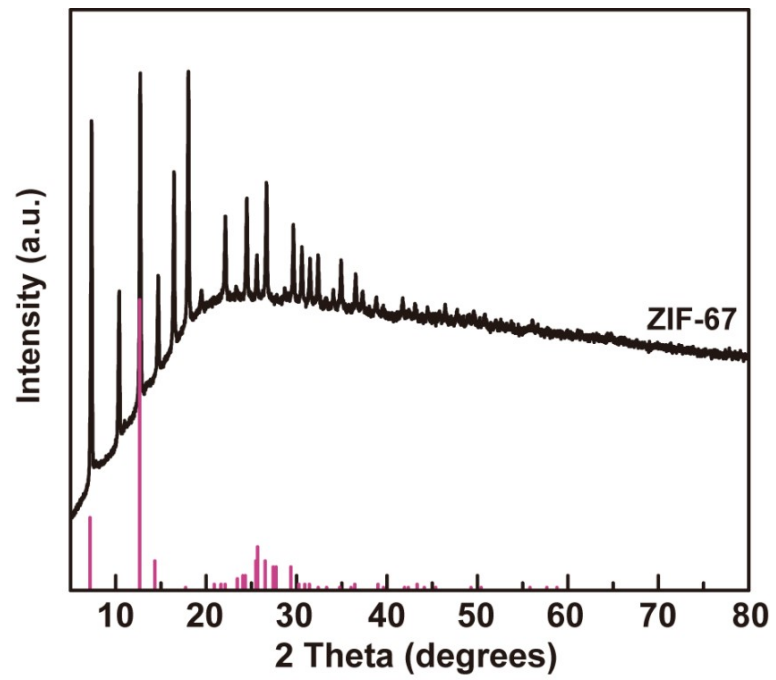


Fig. S3. The X-ray diffraction pattern of ZIF-67.

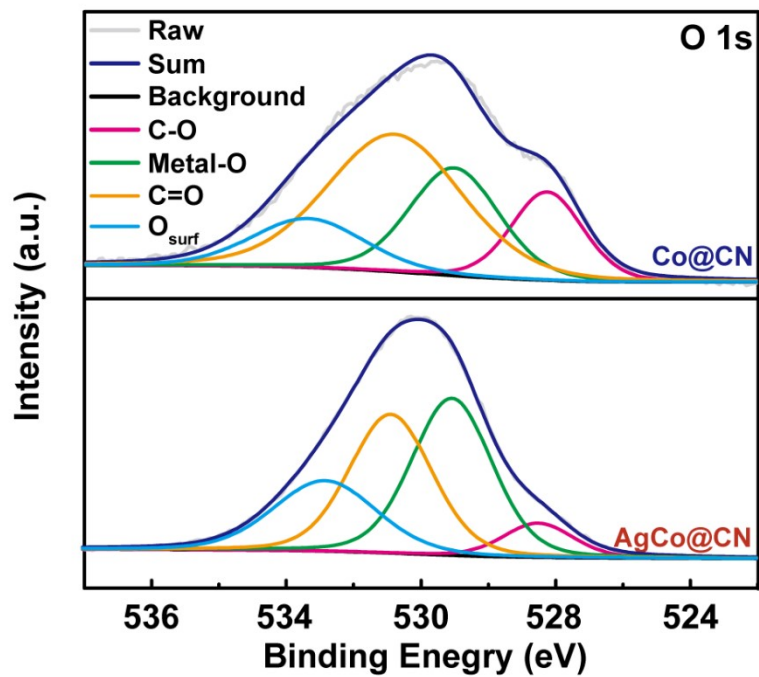


Fig. S4. High-resolution of O 1s spectra of AgCo@CN and Co@CN.

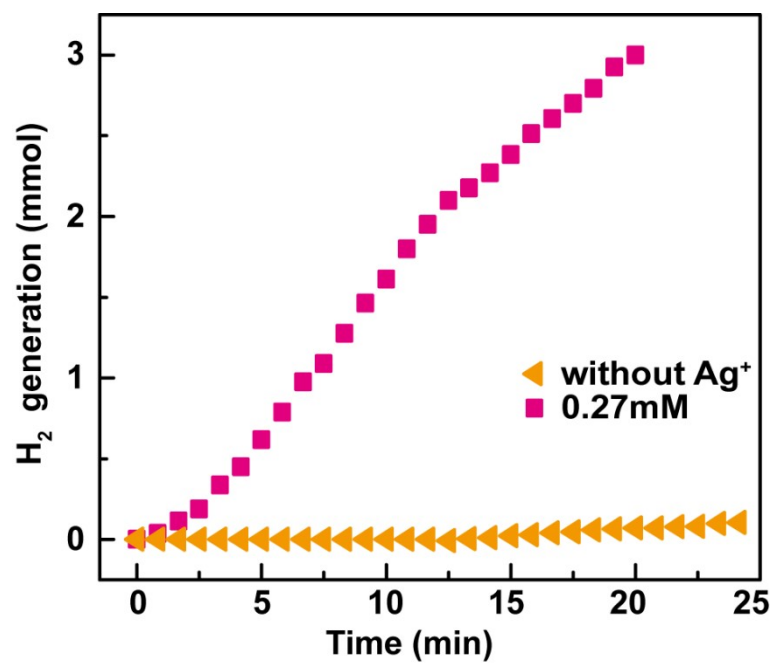


Fig. S5. Hydrolytic dehydrogenation behavior of AB with 0.27 mM and without Ag precursor.

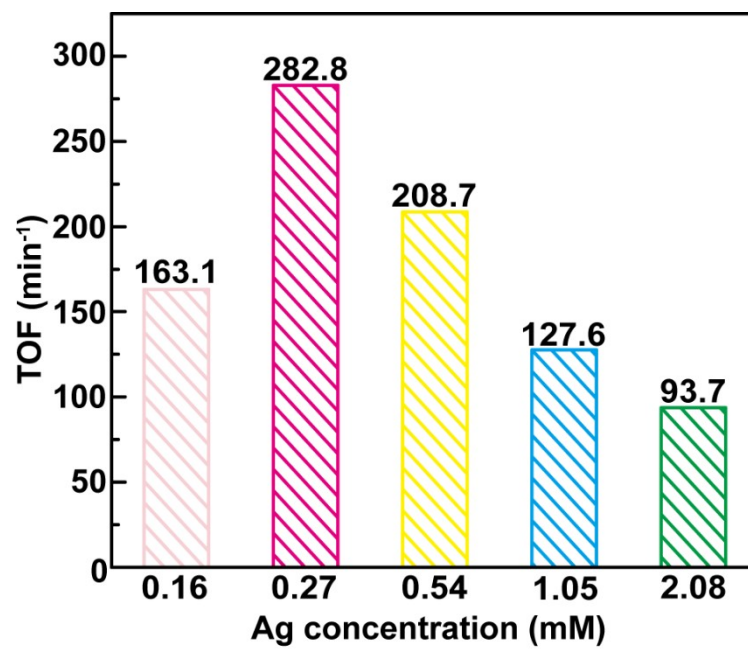


Fig. S6. The TOF values of AB hydrolysis over AgCo@CN with different Ag concentrations.

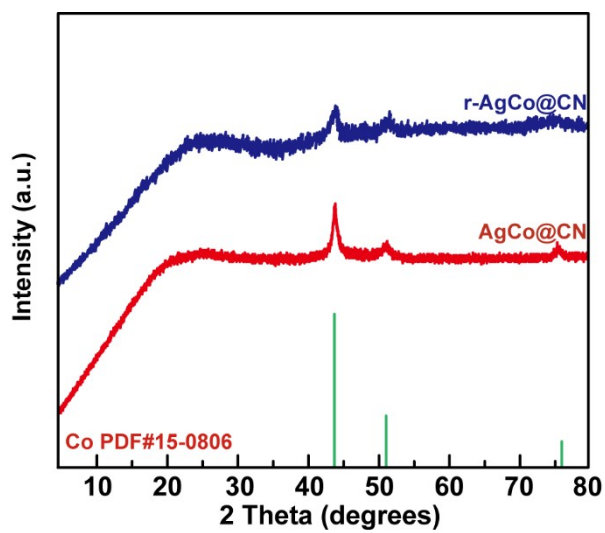


Fig. S7. XRD patterns of the AgCo@CN and r-AgCo@CN catalysts.

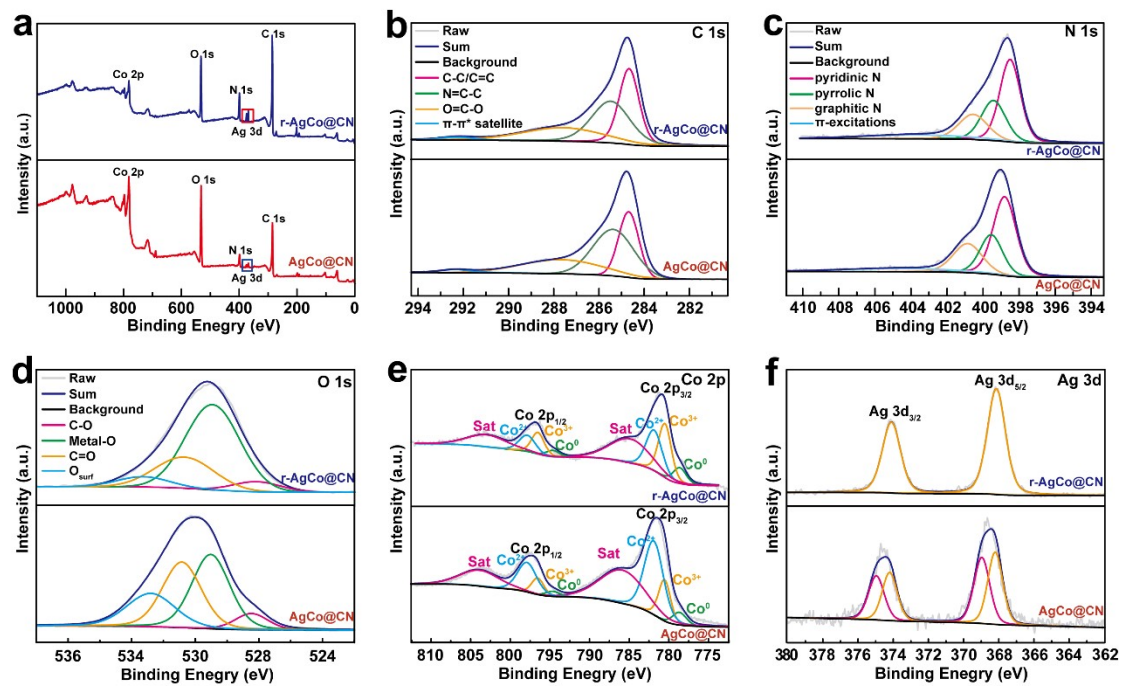


Fig. S8. (a) XPS survey spectra, high-resolution of (b) C 1s, (c) N 1s, (d) O 1s, (e) Co 2p and (f) Ag 3d spectra of AgCo@CN and r-AgCo@CN.

Table S1. Atomic ratios of the elements in AgCo@CN determined by XPS.

Sample	C (%)	N (%)	O (%)	Co (%)	Ag (%)
AgCo@CN	50.80	8.19	30.14	10.53	0.27
					(1.57 wt%)

Table S2. Co 2p Binding energy of the Co@CN, AgCo@CN and r-AgCo@CN.

Name	Type	Binding Energy (eV)		
		Co@CN	AgCo@CN	r-AgCo@CN
Co 2p _{3/2}	Co ⁰	778.7	778.7	778.7
	Co ³⁺	780.5	780.5	780.5
	Co ²⁺	781.9	781.9	781.9
	Sat	785.5	785.9	785.0
Co 2p _{1/2}	Co ⁰	794.7	794.7	794.7
	Co ³⁺	796.5	796.5	796.5
	Co ²⁺	797.9	797.9	797.9
	Sat	803.0	803.9	803.0

Table S3. Catalytic activity for Ag-based catalysts in the hydrolysis of AB.

Catalysts	T (°C)	Ag/AB or Metal/AB (mol/mol, $\times 10^{-3}$)	TOF (min^{-1})	E_a ($\text{kJ}\cdot\text{mol}^{-1}$)	Refs.
Ag@Ni/G	25	0.05 (Metal/AB)	77	49.56	1
Ag _{0.3} Co _{0.7} /PAMAM	25	0.033 (Metal/AB)	15.84	35.66	2
Ag/C/Ni	25	0.022 (Metal/AB)	5.32	39.81	3
Ag ₁ Pd ₄ @UIO-66- NH ₂	25	0.0125(Metal/AB)	90	51.77	4
NiAgPd/C	21	0.012(Metal/AB)	93.8	38.36	5
Ag@CoFe/graphene	25	0.05(Metal/AB)	82.9	37.29	6
AgCo@CN	25	0.00135(Ag/AB)	282.8	31.5	This work

References

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