

## MOF-derived CuCo(O)<sub>2</sub>@ carbon-nitrogen framework as an efficient synergistic catalyst for hydrolysis of ammonia borane

Yao Yuan,<sup>a</sup> Xiaoyu Chen,<sup>a</sup> Xing Zhang,<sup>a</sup> Zumin Wang<sup>\*b</sup> and Ranbo Yu<sup>\*ac</sup>

<sup>a</sup> Department of Physical Chemistry, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China.

<sup>b</sup> State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, 1 North 2nd Street, Zhongguancun, Haidian District, Beijing 100190, China.

<sup>c</sup> Key Laboratory of Advanced Material Processing & Mold (Ministry of Education), Zhengzhou University, Zhengzhou 450002, China.

Email: [ranboyu@ustb.edu.cn](mailto:ranboyu@ustb.edu.cn); [wangzm@ipe.ac.cn](mailto:wangzm@ipe.ac.cn)

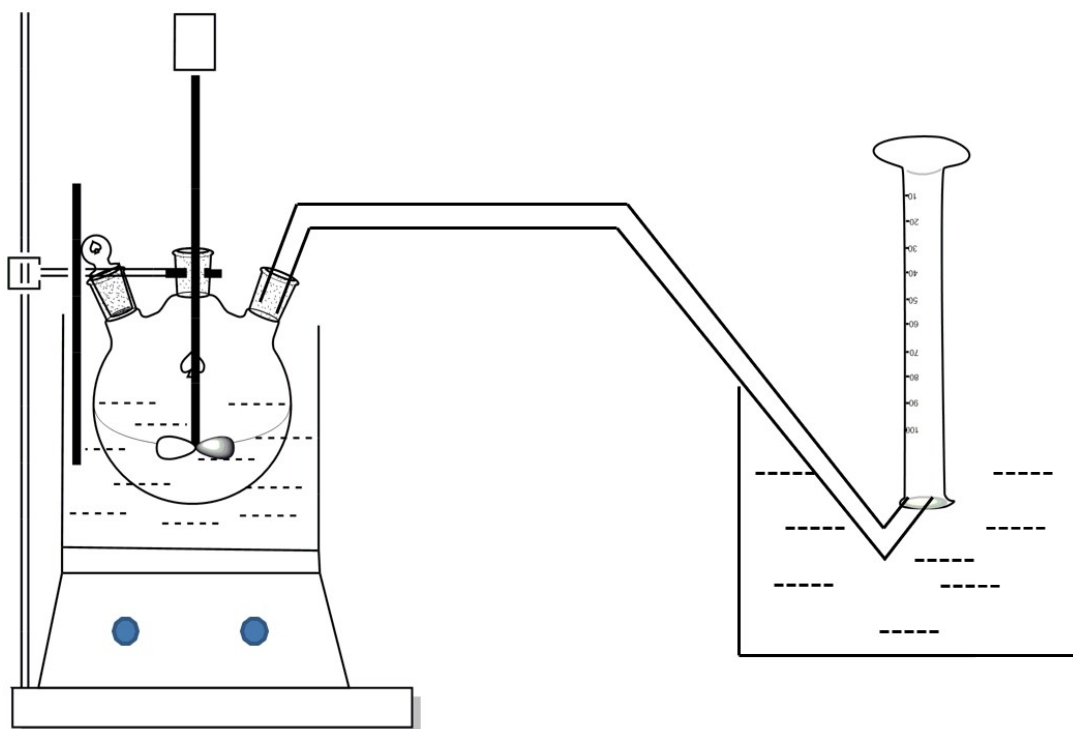
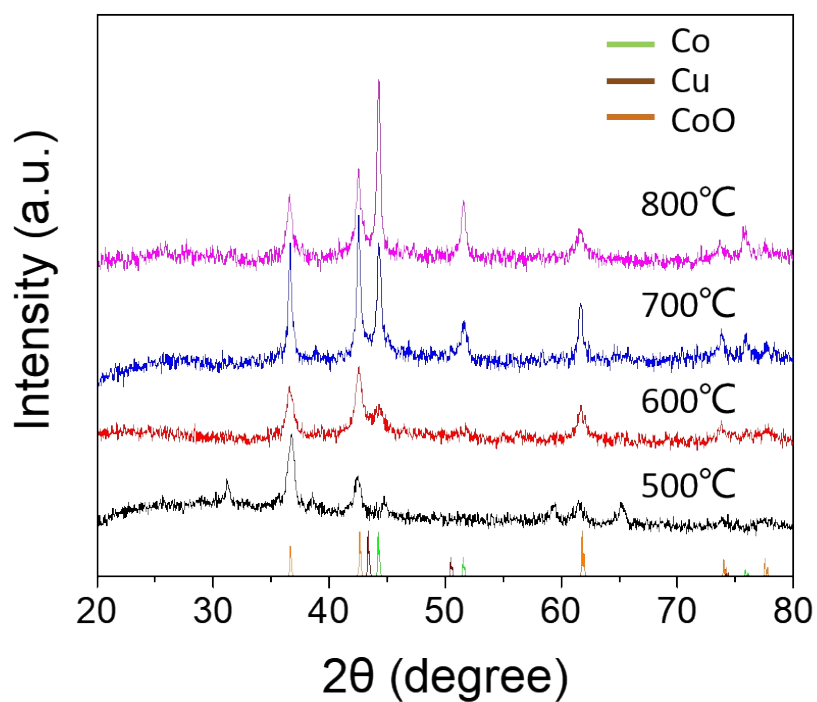


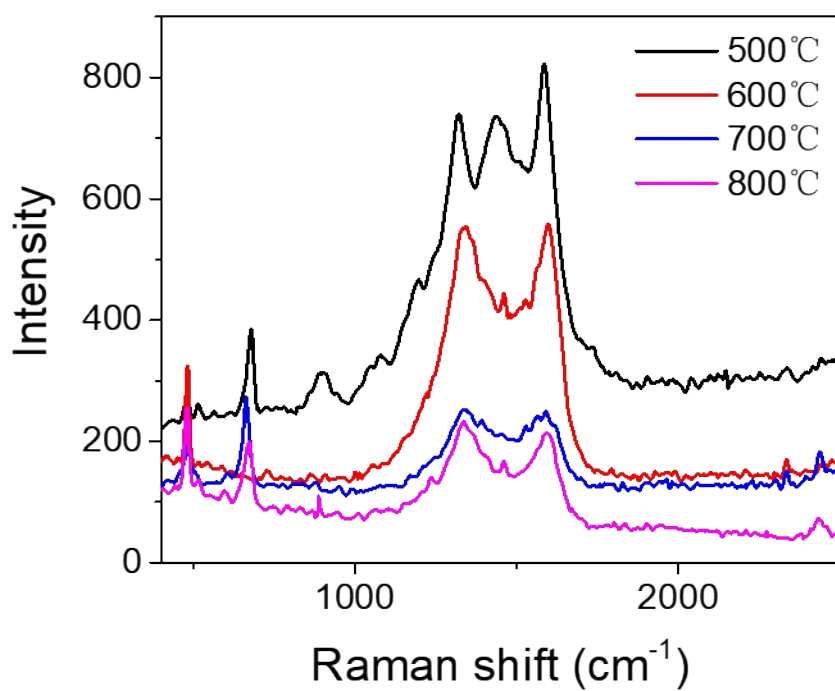
Fig S1 Catalytic test equipment diagram

**Table S1 Element contents analysis of different Samples**

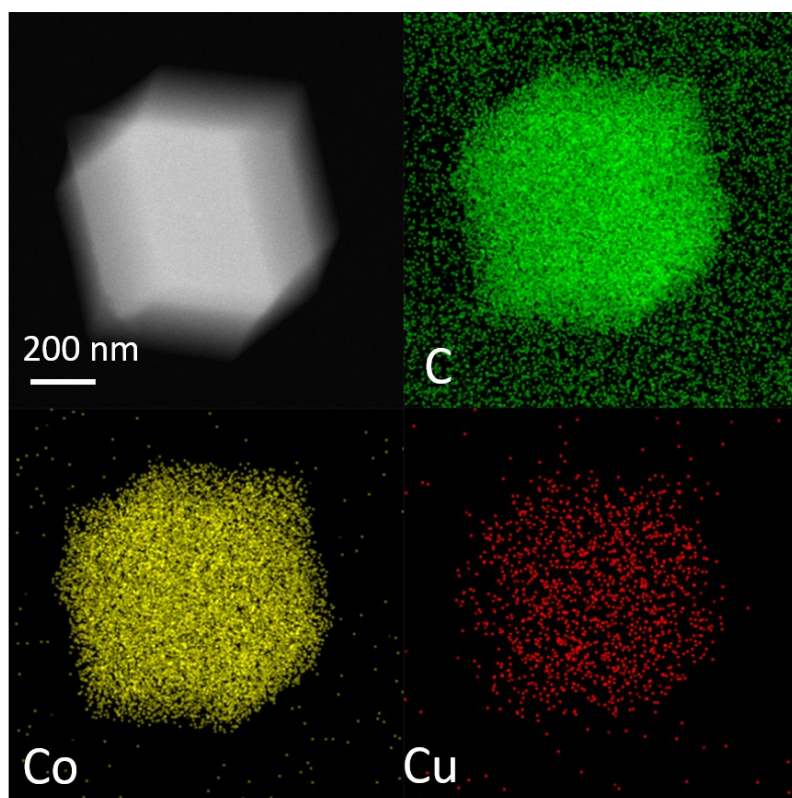
Sample	ICP	
	Cu(wt%)	Co(wt%)
Co(O)@CN	0	42.86
CuCo(O)@CN-I	1.50	35.00
CuCo(O)@CN-II	5.19	42.38
CuCo(O)@CN-III	5.14	53.06



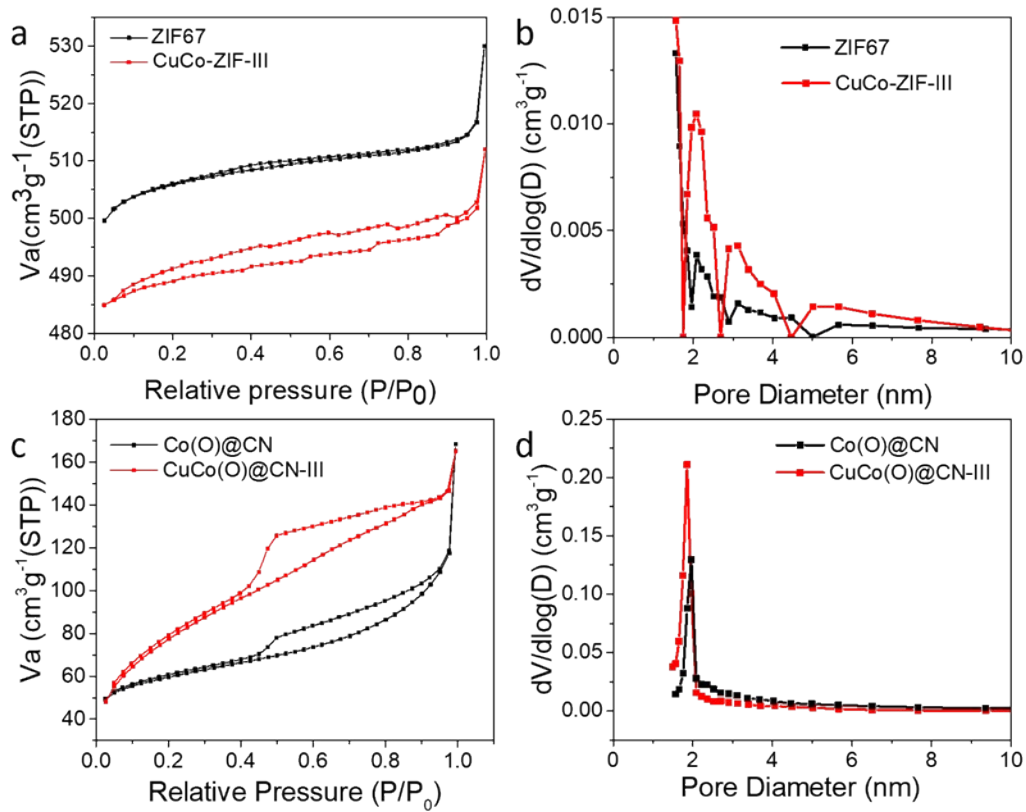
**Fig S2 XRD of samples obtained by calcination at different temperatures**



**Fig S3** Raman spectra of samples obtained by calcination at different temperatures



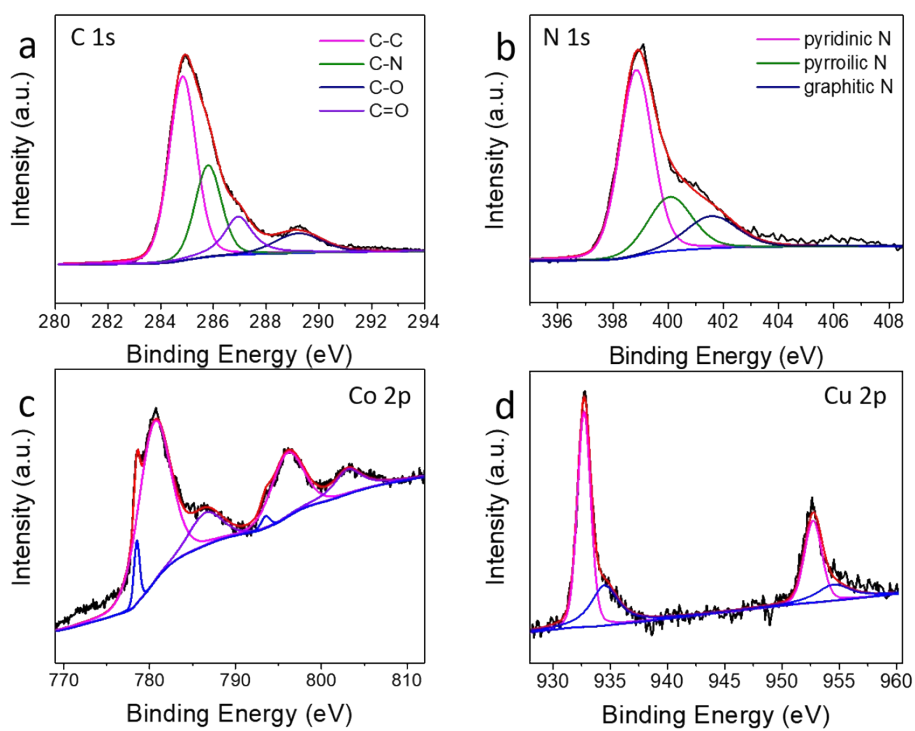
**Fig S4** STEM elemental mapping of CuCo-ZIF-III



**Fig S5 (a)  $\text{N}_2$  adsorption-desorption isotherms (b) pore size distribution curves of ZIF-67 and CuCo-ZIF-III (c)  $\text{N}_2$  adsorption-desorption isotherms (d) pore size distribution curves of Co(O)@CN and CuCo(O)@CN-III**

**Table S2 Specific surface area and Pore volume of different Samples**

Sample	Specific surface area ( $\text{m}^2 \text{g}^{-1}$ )	Pore volume ( $\text{m}^3 \text{g}^{-1}$ )
ZIF67	1742	0.8159
CuCo-ZIF-III	1694	0.7939
Co(O)@CN	209.3	0.2609
CuCo(O)@CN-III	380.1	0.2498



**Fig S6 The XPS pattern of CuCo (O)@CN-III after catalytic reaction: (a) C1s; (b) N1s; (c) Co2p; (d)Cu2p**

**Table S3 Catalytic activities of different catalysts used for the hydrolytic dehydrogenation of AB at room temperature**

catalyst	H <sub>2</sub> generation Rate (mL·min <sup>-1</sup> g <sup>-1</sup> )	TOF (mol H <sub>2</sub> ·(mol cat) <sup>-1</sup> min <sup>-1</sup> )	Ea (kJ mol <sup>-1</sup> )	Reference
CuCo (O)@CN-III	4524	12.39	33.84	<b>This work</b>
Co <sub>0.52</sub> Cu <sub>0.48</sub>	2179	3.4	37.3	Int. J. Hydrogen Energy 42 (2017) 30691–30703.
Cu <sub>0.64</sub> Ni <sub>0.36</sub> -TiO <sub>2</sub> (B)NTs	5763.86	15.9	36.14	Inorg. Chem. Front. 5(2018) 2038–2044.
Cu <sub>0.4</sub> Co <sub>0.6</sub> -BNNFs	3387.1	8.42	21.8	J. Power Sources 431 (2019) 135–143
Cu <sub>0.2</sub> Co <sub>0.8</sub> /HPC	2960	—	47.3	J. Alloy. Comp. 651 (2015) 382–388.
Cu <sub>0.8</sub> Co <sub>0.2</sub> O-GO	—	70.0	—	Angew. Chem. Int. Ed., 55, (2016) 11950–11954
CuCo/graphene	—	9.18	—	J. Mater. Chem. 22 (2012) 10990–10993
Cu <sub>0.5</sub> Ni <sub>0.5</sub> -CN	—	—	39	J. Mater. Chem. A 1 (2013) 14790–14796.
Co/SAG	3013	7.17	46.4	RSC Adv. ,5,(2015)13985-13992.
Ni NPs/C	—	8.8	—	J. Am. Chem. Soc., 132, (2010) 1468-1469.
In-situ Fe <sub>1-x</sub> Ni <sub>x</sub> NPs	—	10.9	—	J. Power Sources 194,(2009) 478-481.
Co-Co <sub>3</sub> O <sub>4</sub> /carbon dots	6816	17.93	40	J. Energy Chem., 48 (2020) 43–53.
Co-CoO <sub>x</sub> @NCS-	5562	13.58	46.37	ACS Sustainable Chem. Eng. 7 (2019), 9782-9792.
Co@N-C	—	5.6	31	Catal. Sci. Technol., 6, (2016) 3443–3448.
CuCo@MIL-101	—	19.6	—	Catal. Sci. Technol., 5, (2015)525–530.
Cu-Co/PDDA-HNTs	—	30.8	36.15	Appl. Surf. Sci., 427, (2018)106–113.
Co/hydroxyapatite	2200	4.54	50	Catal. Today, 183, (2012)17–25.
Cu <sub>6</sub> Fe <sub>0.8</sub> Co <sub>3.2</sub> @MIL-101	—	23.2	37.1	Int. J. Hydrogen Energy (2019)10.1016/j.ijhydene.2019.06.075
Co-Mo-B nanoparticles	5818	—	59.3	Int. J. Hydrogen Energy, 44,(2019)23267-23276
Co/NPCNW	2638	7.29	25.4	Mater. Horiz., 4, (2017) 268–273.

---

Co@NMC	—	—	41.6	J. Power Sources, 399, (2018)89–97.
Co@N-C	—	8.4	36.1	Langmuir, 35, (2019) 671–677.

---