## Porous nitrogen-doped carbon-immobilized bimetallic nanoparticles as highly efficient catalysts for hydrogen generation from hydrolysis of ammonia borane

Lingling Guo, Xiaojun Gu,\* Kai Kang, Yanyan Wu, Jia Cheng, Penglong Liu, Haiquan Su\*

Inner Mongolia Key Laboratory of Coal Chemistry, School of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, Inner Mongolia, China

E-mail addresses: xiaojun.gu@yahoo.com; haiquansu@yahoo.com



Fig. S1 EDS of (a) AuCo/NXC-1, (b) AuCo/NXC-2 and (c) AuCo/NXC-3 (Au/Co = 1/7).



Fig. S2 EDS of (a) AuCo/C<sub>3</sub>N<sub>4</sub>-1, (b) AuCo/C<sub>3</sub>N<sub>4</sub>-2 and (c) AuCo/C<sub>3</sub>N<sub>4</sub>-3 (Au/Co = 1/7).



**Fig. S3** Representative TEM images of (a, b) AuCo/XC-1, (c, d) AuCo/XC-2 and (e, f) AuCo/XC-3 (Au/Co = 1/7).



Fig. S4 EDS of (a) AuCo/XC-1, (b) AuCo/XC-2 and (c) AuCo/XC-3 (Au/Co = 1/7).



**Fig. S5** XRD patterns of (a) AuCo/NXC-1, (b) AuCo/NXC-2 and (c) AuCo/NXC-3; (d) AuCo/NXC-1, (e) AuCo/NXC-2 and (f) AuCo/NXC-3 after heat treatment at 873 K for 4 h in Ar atmosphere; (g) AuCo/NXC-3 after heat treatment at 1173 K for 4 h in Ar atmosphere.



**Fig. S6** XRD patterns of (a)  $AuCo/C_3N_4-1$ , (b)  $AuCo/C_3N_4-2$  and (c)  $AuCo/C_3N_4-3$ ; (d)  $AuCo/C_3N_4-1$ , (e)  $AuCo/C_3N_4-2$  and (f)  $AuCo/C_3N_4-3$  after heat treatment at 873 K for 4 h in Ar atmosphere; (g)  $AuCo/C_3N_4-1$ , (h)  $AuCo/C_3N_4-2$  and (i)  $AuCo/C_3N_4-3$  after heat treatment at 1173 K for 4 h in Ar atmosphere.



**Fig. S7** XRD patterns of (a) AuCo/NXC-1, (b) Au/NXC-1, (c) AuCo/NXC-2, (d) Au/NXC-2, (e) AuCo/NXC-3 and (f) Au/NXC-3.



Fig. S8 XRD patterns of (a)  $AuCo/C_3N_4-1$ , (b)  $Au/C_3N_4-1$ , (c)  $AuCo/C_3N_4-2$ , (d)  $Au/C_3N_4-2$ , (e)  $AuCo/C_3N_4-3$  and (f)  $Au/C_3N_4-3$ .



Fig. S9 XRD patterns of (a)  $AuNi/C_3N_4-1$ , (b)  $AuNi/C_3N_4-2$ , (c)  $AuNi/C_3N_4-3$ , (d) AuNi/NXC-1, (e) AuNi/NXC-2 and (f) AuNi/NXC-3.



Fig. S10 IR spectra of (a) NXC, (b) AuCo/NXC-1, (c) AuCo/NXC-2 and (d) AuCo/NXC-3.



Fig. S11 IR spectra of (a)  $C_3N_4$ , (b)  $AuCo/C_3N_4$ -1, (c)  $AuCo/C_3N_4$ -2 and (d)  $AuCo/C_3N_4$ -3.



**Fig. S12** N<sub>2</sub> sorption isotherms of (a) NXC, (b) AuCo/NXC-1, (c) AuCo/NXC-2 and (d) AuCo/NXC-3 (Au/Co = 1/7) at 77 K.



Fig. S13 N<sub>2</sub> sorption isotherms of (a)  $C_3N_4$ , (b)  $AuCo/C_3N_4$ -1, (c)  $AuCo/C_3N_4$ -2 and (d)  $AuCo/C_3N_4$ -3 (Au/Co = 1/7) at 77 K.



Fig. S14  $N_2$  sorption isotherms of (a) NXC, (b) AuNi/NXC-1, (c) AuNi/NXC-2 and (d) AuNi/NXC-3 (Au/Co = 1/7) at 77 K.



Fig. S15 XPS spectra for (a, b)  $AuCo/C_3N_4-1$ , (c, d)  $AuCo/C_3N_4-2$  and (e, f)  $AuCo/C_3N_4-3$  (Au/Co = 1/7).

Catalyst	TOF	Ref.
	(mol <sub>H2</sub> ·mol <sub>cat</sub> -	
	$^{1}\cdot min^{-1}$ )	
AuCo/NXC-1	42.1	This work
AuCo/NXC-2	7.2	This work
AuCo/NXC-3	12.6	This work
$AuCo/C_3N_4-1$	30.6	This work
$AuCo/C_3N_4-2$	6.4	This work
$AuCo/C_3N_4-3$	14.7	This work
AuCo/XC-1	31.6	This work
AuCo/XC-2	1.6	This work
AuCo/XC-3	7.2	This work
Au-Co@CN with	48.28	10
light		
Au-Co@CN	28.4	10
Pd@Co/graphene	40.9	9(d)
Ru@Co/graphene	40.46	7(o)
Co/PEI-GO	39.9	19(d)
In situ Co	39.8	19(a)
Co(0) nanoclusters	25.7	22(a)
AuCo@MIL-101	23.5	20
CuCo@MIL-101	19.6	9(e)
Cu@Co	15	7(h)
Au@Co	13.7	7(d)
Cu@FeCo	10.5	22(b)
Ag@Co/graphene	10.23	19(c)
Co/hydroxyapatite	4.54	24(b)
Co/Al <sub>2</sub> O <sub>3</sub>	2.08	24(a)

**Table S1** TOF and  $E_a$  values for hydrolysis of AB catalysed by differentcatalysts at 298 K.



Fig. S16 Plots of time versus volume of  $H_2$  generated from aqueous  $NH_3BH_3$  (0.276 M, 6.2 mL) over AuNi/NXC-3, AuNi/NXC-1 and AuNi/NXC-2 at room temperature.



Fig. S17 Plots of time versus volume of  $H_2$  generated from aqueous  $NH_3BH_3$  (0.276 M, 6.2 mL) over  $AuNi/C_3N_4$ -1,  $AuNi/C_3N_4$ -3 and  $AuNi/C_3N_4$ -2 at room temperature.



Fig. S18 Plots of time versus volume of  $H_2$  generated from aqueous  $NH_3BH_3$  (0.276 M, 6.2 mL) over AuCo/NXC-1 with different mole ratio of Au/Co: (a) 1:7; (b) 1:3; (c) 1:1.



Fig. S19 Plots of time versus volume of  $H_2$  generated from aqueous  $NH_3BH_3$  (0.276 M, 6.2 mL) over AuCo/C<sub>3</sub>N<sub>4</sub>-1 with different mole ratio of Au/Co: (a) 1:7; (b) 1:3; (c) 1:1.



Fig. S20 plots of time versus volume of  $H_2$  generated from aqueous  $NH_3BH_3$  (0.276 M, 6.2 mL) over AuCo/NXC-3 with different mole ratio of Au/Co: (a) 1:7; (b) 1:3; (c) 1:1.



Fig. S21 plots of time versus volume of  $H_2$  generated from aqueous NH<sub>3</sub>BH<sub>3</sub> (0.276 M, 6.2 mL) over AuCo/C<sub>3</sub>N<sub>4</sub>-3 with different mole ratio of Au/Co: (a) 1:7; (b) 1:3; (c) 1:1.



**Fig. S22** Plots of time versus volume of  $H_2$  generated from aqueous  $NH_3BH_3$  (0.276 M, 6.2 mL) and Arrhenius plots and TOF values of  $NH_3BH_3$  dehydrogenation over (a, b) AuCo/C<sub>3</sub>N<sub>4</sub>-1, (c, d) AuCo/C<sub>3</sub>N<sub>4</sub>-2, and (e, f) AuCo/C<sub>3</sub>N<sub>4</sub>-3 (Au/Co = 1/7) at different temperatures.