Supporting Information

Experimental

Reagents and materials

Ethylenediaminetetraacetic acid disodium cobalt salt hydrate (Na₂CoEDTA), Hexachloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, 99.9 %), Ammonia borane (NH₃BH₃, 98 %), sodium hydroxide (NaOH) were purchased from Aladdin. Deuterium oxide (D₂O) was obtained from Innochem. All other reagents were commercially available and used without further purification.

Characterizations

The morphology and structure of the samples were characterized using transmission electron microscopy (TEM) on a JEOL JEM-2100 FFEGTEM. 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 Ka radiation. X-ray photoelectron spectroscopy (XPS) spectra were obtained from an ESCALABMKLL X-ray photoelectron spectrometer using an Al Kα source. The thermo gravimetric analysis (TGA) was measured using Diamond TG/DTA instruments (STA 449C Jupiter, Netzsch) under a nitrogen atmosphere up to 800 °C with a heating rate of 5.0 °C min⁻¹. Surface Areas were determined by BET measurements using an Autosorb-1 Surface Area Analyzers (Quanta chrome Instrument Corporation).

Calculation

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

$$TOF = \frac{P_{atm}/RT}{n_{Pt}t}$$
(S1)

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

The catalysts nearly show zero-order reaction kinetics with respect to ammonia borane in the reaction period. Therefore, the reaction rate law could be described as:

$$r = k$$
 (S2)

where k is the reaction constant.

The KIE was determined on the basis of the reported literature using the eq.(S3)

$$KIE = k_{\rm H} / k_{\rm D} \quad (S3)$$

where k_H is the reaction constant of the reaction in H₂O, k_D is the reaction constant of the reaction in D₂O.



Fig. S1. TGA analysis in air atmosphere for Na₂CoEDTA.



Fig. S2. XRD patterns of Pt@Co₃O₄, Co₃O₄/NC-e, and Pt@NC.



Fig. S3. (a) Nitrogen adsorption-desorption isotherms, and (b) pore size distributions of Co_3O_4/NC and $Pt@Co_3O_4/NC$.



Fig. S4. (a,b) SEM images of Co₃O₄/NC.



Fig. S5. (a,b) SEM images of contrastive sample Pt@Co₃O₄.



Fig. S6. High-resolution Co 2p (a) and O 1s (b) XPS scan of the pure Co_3O_4/NC and $Pt@Co_3O_4/NC$ before and after the reuse test.



Fig. S7. (a) H_2 generation vs time graph under different operating methods for AB hydrolysis at 298 K and (b) the corresponding TOF values of (a).



Fig. S8. (a) Time dependences of hydrogen production from hydrolytic dehydrogenation of AB at varied ultrasonication amplitudes and (b) the corresponding TOF values of (a).



Fig. S9. (a) H_2 generation vs time graph over different catalysts for AB hydrolysis at 298 K and (b) the corresponding TOF values of (a).



Fig. S10. (a) Effect of catalyst loadings on the catalytic activity of $Pt@Co_3O_4/NC$. (b) Corresponding TOF values of (a).

	TOF	E	Deervaling	Retained	Dafa
Catalysts	(min ⁻¹)	Ea (kJ·mol ⁻¹)	times	activity	
				(%)	
Pt@SiO ₂	158.6	53.9	5	-	[1]
Pt@MIL-101	414	40.7	-	-	[2]
Pt(8%)/CCF-500	35	39.2	5	47%	[3]
Pt20/CNT	416.5	48.3	4	40%	[4]
Pt/CNT-10W	558	29	5	68%	[5]
Pt/C	111	-	-	-	[6]
Pt/CNT-P	141.7	-	5	24%	[7]
Pt-CeO ₂	133	-	5	66%	[8]
Pt25@TiO ₂	311	-	3	75%	[9]
Pt/CeO ₂ /RGO	48	-	5	90%	[10]
Pt/CNTs-O-HT	468	-	-	-	[11]
Pd–Pt alloy	51.9	-	5	-	[12]
PtNi@SiO ₂	20.7	54.76	5	73%	[13]
Pt-CoCu@SiO ₂	272.8	51.01	6	-	[14]
$Pt_{0.65}Ni_{0.35}$	44.3	39	-	-	[15]
SiO2@Pt@NGO	324.6	-	6	58%	[16]
Pt-PVP/SiO ₂ (M)	371	46.2	5	-	[17]
Pt-Ru@PVP NPs	308	56.3	5	72%	[18]
Pd-Pt@PVP NPs	125	51.7	5	61%	[19]

Table S1. Comparison of catalytic activity, activation energy, and durability of Pt-based catalysts during the AB hydrolysis.

Pt@Co ₃ O ₄ /NC	2007	32.09	ĨŬ	85%	work
	2867		10		This
Pt@CF-12	139	31	7	24%	[26]
Pt@PC-POPs	55	-	5	-	[25]
Pt/graphene	107	-	5	81.2%	[24]
Pt ₅₈ Ni ₃₃ Au ₉	496	-	5	-	[23]
PtRu	59.6	38.9	5	70%	[22]
NP-Pt ₄₀ Co ₆₀	131	38.8	5	65%	[21]
Co _{0.32} Pt _{0.68} /C	67	41.5	-	-	[20]

References:

[1] Y. Hu, Y. Wang, Z.-H. Lu, X. Chen, L. Xiong, Core–shell nanospheres Pt@SiO2for catalytic hydrogen production, Appl. Surf. Sci. 341 (2015) 185-189.

[2] A. Aijaz, A. Karkamkar, Y.J. Choi, N. Tsumori, E. Rönnebro, T. Autrey, H. Shioyama, Q. Xu, Immobilizing Highly catalytically active Pt nanoparticles inside the pores of metal–organic framework: a double solvents approach, J. Am. Chem. Soc. 134(34) (2012) 13926-13929.

[3] M. Yuan, Z. Cui, J. Yang, X. Cui, M. Tian, D. Xu, J. Ma, Z. Dong, Ultrafine platinum nanoparticles modified on cotton derived carbon fibers as a highly efficient catalyst for hydrogen evolution from ammonia borane, Int. J. Hydrogen Energy 42(49) (2017) 29244-29253.

[4] J. Zhang, C. Chen, S. Chen, Q. Hu, Z. Gao, Y. Li, Y. Qin, Highly dispersed Pt nanoparticles supported on carbon nanotubes produced by atomic layer deposition for

hydrogen generation from hydrolysis of ammonia borane, Catal Sci Technol 7(2) (2017) 322-329.

[5] W. Chen, W. Fu, G. Qian, B. Zhang, D. Chen, X. Duan, X. Zhou, Synergistic Pt-WO₃ dual active sites to boost hydrogen production from ammonia borane, iScience 23(3) (2020) 100922.

[6] M. Chandra, Q. Xu, Room temperature hydrogen generation from aqueous ammonia-borane using noble metal nano-clusters as highly active catalysts, J. Power Sources 168(1) (2007) 135-142.

[7] W. Chen, X. Duan, G. Qian, D. Chen, X. Zhou, Carbon nanotubes as support in the platinum-catalyzed hydrolytic dehydrogenation of ammonia borane, ChemSusChem 8(17) (2015) 2927-2931.

[8] X. Wang, D. Liu, S. Song, H. Zhang, Synthesis of highly active Pt–CeO2 hybrids with tunable secondary nanostructures for the catalytic hydrolysis of ammonia borane, Chem. Commun. 48(82) (2012) 10207-10209.

[9] M.A. Khalily, H. Eren, S. Akbayrak, H.H. Susapto, N. Biyikli, S. Özkar, M.O. Guler, Facile synthesis of three-dimensional Pt-TiO2 nano-networks: a highly active catalyst for the hydrolytic dehydrogenation of ammonia–borane, Angew. Chem. Int. Ed. 55(40) (2016) 12257-12261.

[10] X. Wang, D. Liu, S. Song, H. Zhang, Graphene oxide induced formation of Pt– CeO2 hybrid nanoflowers with tunable CeO2 thickness for catalytic hydrolysis of ammonia borane, Chem–Eur J 19(25) (2013) 8082-8086.

[11] W. Chen, J. Ji, X. Duan, G. Qian, P. Li, X. Zhou, D. Chen, W. Yuan, Unique

reactivity in Pt/CNT catalyzed hydrolytic dehydrogenation of ammonia borane, Chem. Commun. 50(17) (2014) 2142-2144.

[12] Z. Zhang, Y. Jiang, M. Chi, Z. Yang, C. Wang, X. Lu, Electrospun polyacrylonitrile nanofibers supported alloyed Pd–Pt nanoparticles as recyclable catalysts for hydrogen generation from the hydrolysis of ammonia borane, RSC Adv. 5(114) (2015) 94456-94461.

[13] X. Qi, X. Li, B. Chen, H. Lu, L. Wang, G. He, Highly active nanoreactors: patchlike or thick Ni coating on Pt nanoparticles based on confined catalysis, ACS Appl. Mater. Interfaces 8(3) (2016) 1922-1928.

[14] Y. Ge, Z.H. Shah, X.-J. Lin, R. Lu, Z. Liao, S. Zhang, Highly efficient Pt decorated CoCu bimetallic nanoparticles protected in silica for hydrogen production from ammonia–borane, ACS Sustainable Chem. Eng. 5(2) (2017) 1675-1684.

[15] X. Yang, F. Cheng, J. Liang, Z. Tao, J. Chen, PtxNi1-x nanoparticles as catalysts for hydrogen generation from hydrolysis of ammonia borane, Int. J. Hydrogen Energy 34(21) (2009) 8785-8791.

[16] W. Ye, Y. Ge, Z. Gao, R. Lu, S. Zhang, Enhanced catalytic activity and stability of Pt nanoparticles by surface coating of nanosized graphene oxide for hydrogen production from hydrolysis of ammonia–borane, Sustainable Energy & Fuels 1(10) (2017) 2128-2133.

[17] J.-T. Du, H. Niu, H. Wu, X.-F. Zeng, J.-X. Wang, J.-F. Chen, PVP-stabilized platinum nanoparticles supported on modified silica spheres as efficient catalysts for hydrogen generation from hydrolysis of ammonia borane, Int. J. Hydrogen Energy

46(49) (2021) 25081-25091.

[18] M. Rakap, Hydrogen generation from hydrolysis of ammonia borane in the presence of highly efficient poly(N-vinyl-2-pyrrolidone)-protected platinum-ruthenium nanoparticles, Appl. Catal., A 478 (2014) 15-20.

[19] M. Rakap, Poly(N-vinyl-2-pyrrolidone)-stabilized palladium-platinum nanoparticles-catalyzed hydrolysis of ammonia borane for hydrogen generation, J. Power Sources 276 (2015) 320-327.

[20] X. Yang, F. Cheng, Z. Tao, J. Chen, Hydrolytic dehydrogenation of ammonia borane catalyzed by carbon supported Co core–Pt shell nanoparticles, J. Power Sources 196(5) (2011) 2785-2789.

[21] Q. Zhou, C. Xu, Nanoporous PtCo/Co₃O₄ composites with high catalytic activities toward hydrolytic dehydrogenation of ammonia borane, J. Colloid Interface Sci. 508 (2017) 542-550.

[22] Q. Zhou, C. Xu, Nanoporous PtRu alloys with unique catalytic activity toward hydrolytic dehydrogenation of ammonia borane, Chemistry – An Asian Journal 11(5)
(2016) 705-712.

[23] J.-X. Kang, T.-W. Chen, D.-F. Zhang, L. Guo, PtNiAu trimetallic nanoalloys enabled by a digestive-assisted process as highly efficient catalyst for hydrogen generation, Nano Energy 23 (2016) 145-152.

[24] D. Ke, J. Wang, H. Zhang, Y. Li, L. Zhang, X. Zhao, S. Han, Fabrication of Pt– Co NPs supported on nanoporous graphene as high-efficient catalyst for hydrolytic dehydrogenation of ammonia borane, Int. J. Hydrogen Energy 42(43) (2017) 2661726625.

[25] H. Zhao, G. Yu, M. Yuan, J. Yang, D. Xu, Z. Dong, Ultrafine and highly dispersed platinum nanoparticles confined in a triazinyl-containing porous organic polymer for catalytic applications, Nanoscale 10(45) (2018) 21466-21474.

[26] J.R. Deka, C.S. Budi, C.-H. Lin, D. Saikia, Y.-C. Yang, H.-M. Kao, Carboxylic acid functionalized cage-type mesoporous silica FDU-12 as support for controlled synthesis of platinum nanoparticles and their catalytic applications, Chem–Eur J 24(51) (2018) 13540-13548.